THE PROCEEDINGS OF
THE PHYSICAL SOCIETY

VOL. 49, PART 5 *September* 1, 1937 NO. 275

THE OPTICAL GLASSWORKS AT BENEDIKTBEUERN

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Address given before the Physical Society at Burlington House,
3 *December* 1936

THE history of the manufacture of glass produced specifically for optical use covers the short span of just over 130 years. Although the discovery of the achromatic lens, by Chester Moor Hall between 1729 and 1733 and its development by Dolland from 1758 onwards, was the first radical improvement in optics since the discovery of spectacles about the year 1300, progress was limited owing to the difficulty of obtaining suitable glass, and particularly flint glass, of adequate homogeneity.

Prof. von Rohr has rendered great service to the cause of historical research by his investigations on optics, and it was through a study of his writings that I learnt of Fraunhofer's work at Benediktbeuern. During a visit paid last summer to the Deutsches Museum at Munich, I noticed a photograph of the old works, and determined later to visit this historic spot; but this is getting ahead of our story, and we must revert to Munich in the year 1801, when the French Government were requiring a military map of Bavaria, but were encountering difficulties owing to the lack of suitable surveying instruments. About this time, an artillery officer, Georg Reichenbach, had journeyed to England to study machine construction and foundry work, and had seen some of the important businesses producing mathematical instruments. He determined to set up such a works in Bavaria, so as to make his country independent of foreign supply, and to train a body of highly skilled artisans. In 1802, Reichenbach joined the clever mechanic and watchmaker, Liebherr, who already possessed a small workshop, and two years later they formed a partnership with Geheimreferendar Joseph Utzschneider, a man of affairs no longer active in the service of the State, and possessing interests in cloth and leather works.

It was on 20 August 1804, that the "Mathematical Mechanical Institute Reichenbach, Utzschneider and Liebherr" came into being, and the manufacture of instruments commenced. The concern very soon found itself in difficulties owing to lack of suitable lenses, so Joseph Niggl, a skilful but empirically trained optician, was engaged. However, lenses could not be made without suitable glass, and in particular flint glass, which was almost unprocurable in France and Germany, and could only be obtained with difficulty in England. The success of the new undertaking was at stake, and the energetic Utzschneider set himself to solve the problem. He visited various well-known South German opticians, but it was not until he got in touch through the Swiss J. S. Gruner with another Swiss, by name Guinand, that any prospects of success appeared likely. Pierre Louis Guinand, born on 20 April 1748, was brought up as a skilled cabinet maker and specialized in the production of clock cases. Later he became acquainted with the work of casting metals, and as a hobby interested himself in making spectacles and telescopes. Deciding to make his own instruments, he was faced with the necessity of procuring suitable lenses, and decided to experiment with the production of glass. An account of his experiences is contained in a memorandum prepared by him for Utzschneider in 1804. We learn that after studying books on chemistry and consulting the encyclopaedia, he started in 1774 to make small trial melts using some 3–4 lb. of materials, trying variations in composition and temperature, and recording systematically the results. After 13 years' experimenting, he decided that the scale of his operations was not big enough to achieve results, and in 1787 constructed a furnace in which he could make melts weighing up to 200 lb. He had moved his residence to les Brenets (West Switzerland) in 1781, and purchased a mill with the object of using the water power to drive his glass saws and polishing machines. Owing to lack of means, progress was slow, but it seems that in 1798 he started to improve the homogeneity of his glass by means of stirring, though at first without much success. However, he must have made progress, as he felt sufficiently confident to send samples to French opticians, and later to approach the Elector Palatine of Bavaria with proposals to deliver flint glass free from striae. In 1805, Utzschneider and Guinand came into direct contact and met in Aarau. An agreement was made by which Guinand should carry out some trial melts at Utzschneider's expense, and this was done between April and July 1805. Guinand prepared a memorandum on his results—*Memorandum on Making Glass, especially of High Refraction for the Manufacture of Achromatic Telescopes*—which gives us a mass of detail concerning his early trials and those paid for by Utzschneider. It appears that in July of that year, he used for the first time a stirrer consisting of a hollow fireclay tube, moved through the glass by means of an iron hook-ended rod. This was undoubtedly the secret of his success, and to this day forms the essential feature of the process of optical glass manufacture. Samples were sent to Munich for testing, and must have given satisfaction, as Utzschneider visited Guinand at les Brenets in the autumn, entered into an arrangement with him to come to Bavaria, and gave him a handsome sum towards the cost of his journey.

Utzschneider about this time purchased the Benedictine Monastery at Benediktbeuern, with its farm and lands. It lies about 30 miles from Munich, close to the foothills of the Benediktenwand, and is situated in charming country. Founded in the eighth century, supposedly in connection with the activity of Holy Bonifacius in Bavaria, it had been destroyed by the Hungarians in 985, but rebuilt by the Benedictines of Tegernsee in 1031. It became a great centre of art and learning, but fell on evil times in the Thirty Years' War and in 1632 was plundered by the Swedes. In 1803, it was dissolved and for 130 years put to secular use. It covers a large area of ground and embodies the original cloister adjoining the church, another large cloister built at a later date forming the convent buildings, together with extensive farm and other buildings. At the present time, it is occupied partly by the Salesian order as a theological college and partly by a contingent of the Labour Corps.

Doubtless one of the attractions in Utzschneider's mind was the abundant supply of wood for his furnace and he selected the washhouse to serve as his factory, as being suitable for housing Guinand and as having a mill stream running past which could easily be employed to drive the polishing machinery. Later I shall describe the present state of the house and its wooden extension which houses the furnaces.

Guinand brought with him his young second wife, Rosalie, and set to work to build a furnace and to get together the necessary equipment. Some melts were made, though not altogether with success, but Utzschneider seems to have been satisfied with the glass, which was probably tested by Niggl. At any rate, an agreement was drawn up in May 1806, of which the following is a summary of the terms:

(1) Guinand was to work the furnaces himself with the help of his wife and, with a view to maintaining strict secrecy, was only to employ outside labour for non-essential work.

(2) With a view to making use of the whole of the convent buildings, there should be set up a manufactory for achromatic lenses, but crown and flint glass should not be sold in the raw state except in limited quantity to the partnership in Munich, and all the rest should be used for making lenses under Guinand's control at Benediktbeuern.

(3) In addition to the optical glass, a glassworks was to be started for the manufacture of white glass.

(4) Guinand was to receive 500 florins per annum with lodging and fuel, and one-fifth of the profits of the establishment.

(5) As recompense for his discovery, and to bind him to secrecy, Guinand was to receive 500 florins per year for 10 years.

(6) Guinand's wife, Rosalie, was to assist her husband and after his death to receive 200 florins yearly for life; and Guinand was to instruct one of his sons so as to be able to succeed him in the event of his death.

(7) The management of the concern, the engagement of workers and all financial matters were to be continued by Utzschneider, and, in the event of the venture prospering, a furnace was to be erected for the manufacture of cast glass.

The first agreement did not work out altogether as expected, and in February 1807 a second agreement was signed. Whereas the first was entered into by Utzschneider alone on the one part, the partnership at Munich were the contracting parties on the second. Guinand was engaged for 10 years to concern himself only with optics and principally the mounting of objectives. He was to go to Benediktbeuern several times a year to make glass for the partnership, to instruct a person, nominated by Utzschneider, in his methods, and to receive 1600 florins yearly, with furnished house and fuel. The house at Benediktbeuern was to be put at his disposition as and when required, and his travelling expenses paid. At the end of his contract, he was to receive a yearly pension of 800 florins, together with house and fuel (unless he returned to his native country), and in the event of his death, his wife was to receive a pension of 250 florins yearly, provided she did not disclose his secrets.

In point of fact, Guinand did not go to Munich, presumably because it was decided to transfer the manufacture of lenses to Benediktbeuern, and it was thought vital to the Munich partnership that Guinand should make a real success with his glass.

We must now leave glass for the moment and turn to the optical side, of which Niggl was in charge. Utzschneider decided to provide him with an assistant, and after making enquiries, engaged one, Joseph Fraunhofer, then twenty years old. Fraunhofer was born on 16 January 1787, the son of a master glazier at Straubing, and lost both his parents when only 11 years old. Guardians were appointed, and Fraunhofer was apprenticed to a wood turner. The work did not suit him, and it was decided to make him a glass cutter and mirror polisher, to which end he was apprenticed to one, Weichselberger, who seems to have been a stern taskmaster and disciplinarian. In the second year of his apprenticeship, a fortunate accident—the collapse of the house in which he was working and under the ruins of which he was buried—brought him to the notice of the Elector of Bavaria, who gave him a substantial present, part of which he spent in buying himself out of his contract. After trying to make himself independent, he was forced to return to his master. His education, until now, had been very scanty, but a fortunate meeting with Utzschneider at the time of the accident enabled him to begin to study the best books on optics, and he seems to have made full use of his opportunities, for on Niggl's departure from the Munich establishment towards the end of 1807, Fraunhofer was put in charge in his place, and shortly after moved to Benediktbeuern, where Utzschneider had installed a special optical workshop. I cannot say whether this occupied part of the convent washhouse, or whether it was placed elsewhere, but it would seem possible that the former was the case, as the washhouse is a spacious building and bordered on one side by the mill stream, which could easily have been used for driving Guinand's grinding and polishing machinery, as in the case of the water-driven crusher for raw materials.

Fraunhofer set to work with amazing energy for one so young. He had already shown signs of his inventive genius in undertaking the task of converting a grinding machine for spherical into one for aspherical surfaces. Apprentices were engaged and instructed, new methods of manufacture introduced and the business organized to speed up delivery. From the first there was a clash of temperaments between Guinand and Fraunhofer; the former sanguine and optimistic, the latter cold and patient. Fraunhofer expressed dissatisfaction at the quality of Guinand's glass, while Guinand was piqued that a much younger man should criticize his work.

At last Utzschneider had to intervene, and, in spite of Guinand's objections, it was arranged in accordance with the agreement that Fraunhofer should be instructed in Guinand's methods of glass-making (August 1809).

Although we have little information about what was actually done, great strides must have been made in improving the manufacture, as is shown by the price lists of 1811 and 1812, in which are listed hand telescopes with objectives up to 83 mm. in diameter. There is little doubt that the progress was mainly due to Fraunhofer, and it is probable that, apart from increasing the size of the pot from 2 to 4 cwt. content, improvements in technique rather than improvements in principle were the secret of success.

By 1811, Fraunhofer was put in charge of all the work at Benediktbeuern. He had been taken in as junior partner in 1809, and the firm was known as the "Optical Institute of Messrs Utzschneider, Reichenbach and Fraunhofer at Benediktbeuern".

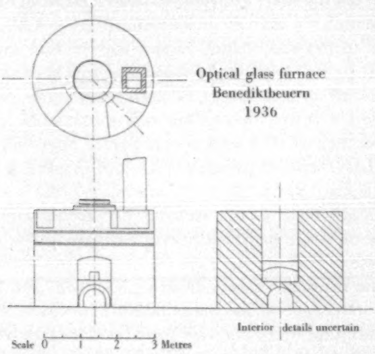
Ever since Fraunhofer's arrival at Benediktbeuern, Guinand had been unsettled, and a letter to his son, Aimé, shows that he had thoughts of returning home. We know that he had a secret arrangement with a young Strahl, who came to Benediktbeuern in 1809, and whom he instructed in his glass-making methods with a view to using his services later on his own account. In 1813 matters came to a head, and in December of that year it was agreed that Guinand should return home the following May, that his pension of 800 florins annually should commence, the payment for 1814 and 1815 being made in advance, that his wife should receive her pension in the event of his death, and that he and his wife should not interest themselves in optics or make or assist others to make glass, failing which their pensions were to cease.

The design of the original furnace built by Guinand and his young wife can only be surmised by reference to the memorandum in which he describes his early efforts, and by an examination of the two furnaces now standing as they were left when the works closed down in the 90's of last century.

Guinand's first large furnace was heated at the side (by wood) and the waste gases could be passed either through a chimney or used partially to warm a subsidiary chamber in which the blocks of glass were flowed out in moulds into discs or prisms. Another chamber adjoining the melting furnace was used for "fritting" (preheating) the raw materials, and on top of the flowing-out chamber was a large box for drying wood. The stirrer was introduced through a hole arranged vertically above the pot and could be rotated by a rope-driven mechanism.

This furnace seems to have given inadequate heat to free the glass from bubbles, particularly in the case of crown glass melts, and a new design had its fire below the pot and was arranged to tilt, so as to allow the glass after stirring to be poured into a suitable mould. The pot was supported on bearers, and was about 18 in. internal diameter and 1 ft. high. As he had trouble with pots breaking, he fixed the melting pot inside an outer pot which was supported at a number of points against the walls of the furnace; the space between the inner and outer pots being filled with sand. Means for stirring were similar to the first furnace and the stirrer could also be moved up and down, so as to increase the mixing effect.

The Benediktbeuern furnaces are circular and have a tunnel running through the bottom which contains the fire grate. The pot was placed in a chamber in the centre of the furnace and rested upon a hearth through which penetrated the flames from the fire grate. At the top of the furnace two sections, resembling slices from a circular cheese, are cut out and were used for filling the pot and viewing the progress of operations. The walls of the hearth are vertical, thus forming a circular chamber, which is closed at the top by means of a circular fire-clay stopper. Each furnace has its own crane for lifting the pots in and out. The stirring mechanism consists of an iron rod affixed to the roof of the building and hanging vertically over the centre of the pot. It is forked at its bottom end and provision made to attach the fire-clay stirrer. Rotation is effected by means of a long arm attached at one end to a crank, which can be rotated, and at the other to the iron rod. To seal the mouth of the furnace, a second circular fire-clay stopper is attached by three adjustable arms to the stirring rod, such that the disc swings just clear of the circular cover slab, in which is a central hole of size appropriate to allow the stirring rod to move. The movement of the stirrer through the glass does not appear to have been capable of any great regulation, and must have depended to some extent upon the speed of rotation of the driving crank.


Optical glass furnace
Benediktbeuern
1936

Although the two existing furnaces must have been erected subsequent to Guinand's original furnace, it seems probable that they were built after Fraunhofer's death. They differ little in principle from Guinand's last furnace, except that the means for tilting to effect pouring of the glass into moulds is not incorporated. We know that Fraunhofer made a practice of making one or two small experimental pots of glass with each full scale melt, and the dimensions of the existing furnaces would not seem adequate for this purpose. It is interesting to note that other successors to Guinand's secret altered the method of stirring in that the stirrer was introduced through the side of the furnace, possibly as making a more convenient arrangement and probably also as it was found desirable to use covered pots for the manufacture of flint glass. The dimensions of the pot used would not appear to have been increased beyond the 4 cwt. size, as the furnace chamber is not big enough to take a larger pot.

The two furnaces described are installed in a wooden building 62 ft. long by 18 ft. wide, adjoining the one-time washhouse. In one corner is a kiln used for "flowing out" lumps of glass recovered after the melting pots had cooled down and their contents broken into suitable sized pieces. A short while ago, the property was purchased by Prof. Walther Küchler, late of Vienna and other universities, and has been converted into a charming residence. The main building is spacious and has three floors and an attic which communicates by stairs with the glasshouse. It seems possible that this was used for building and storing pots. In the basement were stored raw materials and the remains of a crusher driven by a water wheel can still be seen. Realizing the historic interest of the place, Prof. Küchler has been wise enough to have the furnace building left intact, and it is to his services, in preserving what might easily have been scrapped as of no practical value, that I am indebted for my information.

Fraunhofer kept careful records of his melts, and on his deathbed dictated to his friend the Mintdirektor von Leprieur a memorandum describing the manufacture of crown glass. Among his papers is an account of a flint glass melt made in 1814. From these sources we know something of his methods and can compare them with the recollections of one of the workmen employed later under Merz (of whom more anon). Fraunhofer's description runs as follows:

> The following were the methods employed with Flint glass No. 16: On 20 January (1814) the pot was brought to the furnace. The bottom of the outer pot was covered with clean crushed quartz to a depth of about 1″, the inner pot placed inside, and the space between the two filled with similar quartz. The pots were then hung by three irons, which could be adjusted with screws, to the rope of the large crane, such that the inner walls of the pot were set vertically. The siege of the furnace was covered with 1½″ of clay and the pots lowered onto the siege. As the inner wall of the pot hung vertically, it must remain vertical in the furnace when it sank onto the clay bed. The inner wall of the small pot was painted with powdered glass before placing it into the furnace. The furnace was not closed, a cover being placed over the pots. The large and small stoppers were bedded in lime and only one of the inspection holes left open, through which on the 21st a fire of undried wood was lighted. At night the inspection hole was closed by a stopper and in the morning fire was again made; until the morning of the 26th this procedure continued, when a fire was made in the fireholes with undried wood. At night dried wood was charged, so that by the morning of the 27th the furnace was hot enough. On this morning the Potash was prepared and added to the batch. Several days previously the Saltpetre had been mixed with the red lead, to which the Quartz had already been added; and last of all the Potash, in proportions shown in the records, and still so wet as not to be quite fluid. Before the furnace had reached its top temperature, it was glazed with flint glass cullet and this was then removed. At 9.30 in the morning filling of the batch commenced. Only two shovelfulls were filled on at a time, so as not to chill the pot excessively and risk losing it; 8–10 minutes pause took place between fillings. At 7 in the evening the filling was finished and the pot quite full, so that 100 lbs. of glass had to be ladled out. From 11 midday to 9 in the evening the glass was stirred with the cylinder every 8–10 minutes. At 9.30 in the morning of the 28th the glass was skimmed and then stirred till 12 noon, at which hour

the furnace required stoking. At 1 o'clock the cover of the furnace was removed and the glass carefully skimmed, and at 1.45 the fire was again stoked, at first lightly and then more heavily. About 3.30 in the afternoon stirring was again started and continued till 5; it took place every ¼ hour and at first more often; during this period birch wood was used for firing. At 8.30 in the evening preparations were made for the last stages and at 10 stirring began again. The stirrer moved about 1½″ from the pot wall, and was turned evenly backwards and forwards. The glass was fairly fluid. Before the last stirring the glass was again carefully skimmed. At 1.30 a.m. on 29th stirring ceased. The furnace remained open for an hour and the openings were then closed and 5 hours later bushed up with lime and the inner stopper covered with earth so as to slow up the rate of cooling of the furnace.

Fraunhofer's instructions (1826) for making crown glass give some further information about his methods. He stated that a larger furnace was required than when making flint glass. The batch was similar to that used for ordinary white glass, but gave a yellowish green colour and after "flowing out" often devitrified. By raising the chimney flue and thus altering the direction of the flames matters were improved, but the colour was still unsatisfactory and attention was turned to the raw materials. He noted that potash was the most important, and tested its purity by calcining and observing its colour. The selected material was again calcined, dissolved in water and allowed to stand until impurities had settled out. The solution was then poured into a boiler and heated until the neutral salts began to crystallize; the solution was then poured into glazed bottles and allowed to cool and crystallize, the resultant potassium oxide being heated on the day when it was used. The silica was introduced in the form of quartz obtained from the Zillertal (Tirol). It was calcined, cracked in water and the coloured impurities removed; then crushed in the stamp mill and sieved to the desired fineness. The lime needed careful selection and its choice required experience.

The proportioning of the raw materials was considered important, as an excess of lime and potash, though giving a glass free from bubbles, increased the tendency of the resultant glass to weather. It is interesting to note that Fraunhofer discovered that an addition of alumina, though giving rise to poor colour, improved the durability. Crown glass is hard to free from bubbles and small fillings are advised. It is also considered very important to pay particular attention to the firing and not to fill away unless the furnace is at its proper temperature.

Plank, the workman previously referred to, throws some light on the developments since Fraunhofer's time, though procedure seems to have undergone little alteration. It was considered important to dry the wood before firing and this was done in a separate building adjoining the furnace house. Beech wood was considered essential for the furnace and was cut into small pieces to give even firing. Instead of quartz, sand was obtained from Nantesbuch, a small village near Wolfratshausen, and was crushed, washed and sieved. Lead oxide came from abroad and the potash seems to have been obtained locally and purified as before. The pots were made of a mixture of Kassel clay and clay from Kehlheim. Possibly this was a better material than that used by Fraunhofer and obviated the necessity for an outer pot. To the clay was added suitable proportions of broken pots and "flowing-out" moulds.

The furnace nearest the house was used for flints, only one furnace being used at a time. A crew of four men with several boys to assist seems to have been the normal complement. Melts were made at a rate depending upon the demand, but generally one per month; the flints taking 5 days and the crown 8 days, not including the period of about a fortnight during which the furnace was cooling down.

The "flowing-out" furnace was fired with pine wood and heated until the lumps of glass "flowed out" into moulds, whereupon it was sealed and allowed to cool for some 14 days. Unsuitable glass was sent to Munich, where bubbles were ground out, and returned to Benediktbeuern for "flowing-out", the scrap glass being crushed and mixed with the batch.

During the period 1811–14, Fraunhofer not only supervised the glass-making, but was engaged upon a work of fundamental importance—the accurate measurement of the refractive index and dispersion of the meltings made. He hit upon the idea of using the dark lines of the spectrum previously noticed by Wollaston in 1802, and used for his purpose a theodolite. In 1817, he read an important paper before the Munich Academy in which he accounted for 574 of these lines and later was able to determine the length of the corresponding light waves for seven of the most important lines. He was led to this work by the necessity to reduce the secondary chromatism of his lenses and could not tackle the problem satisfactorily until he could measure accurately the optical properties of his glasses. By means of small trial pots which accompanied the full-scale meltings he experimented with different proportions of raw materials and in his paper of 1817 he could describe a pair of flint and crown glasses (Flint 13 and Crown M) which showed considerable improvement in that they possessed a more or less proportionate increase in partial dispersions. Owing to the glass being of poor durability, it was not in fact used commercially.

In 1811, forty-eight people were employed in the works, including five turners, twenty glass polishers, two tube drawers and so on. About this time, the manufacture of spectacle lenses was introduced and continued to persist as a cottage industry after the optical section of the works was transferred to Munich in 1819.

Reichenbach left the partnership in 1814 to found his own workshop for precision instruments, but continued to procure his glass from Benediktbeuern, and in the same year, Guinand left as had been arranged. We hear of him two years later when he endeavoured to persuade Utzschneider to take him back, though without success, as Utzschneider had heard of his attempts to restart his own glass works contrary to the terms of the agreement and refused to reply.

The undertaking was now solely in the hands of Utzschneider and Fraunhofer, and a new partnership was formed, in which Fraunhofer was given a substantial interest. Progress continued to be made in improving the quality of the instruments manufactured, and in increasing the size of the lenses employed. The glass making remained Fraunhofer's sole responsibility, and no one else was allowed to learn its secrets. He looked after the purchases of chemicals and other materials, and was responsible for the whole organization. In 1819, Utzschneider decided to move the optical section of the business to Munich, and sold the convent to the State, retaining only the glasshouse. No doubt it was found inconvenient for visitors to travel the 30 miles from Munich, and possibly the supply of skilled labour presented a difficulty.

Among other problems tackled by Fraunhofer was the question of glass durability, which he tested by using sulphuric and nitric acids. Polished glass surfaces were preferably treated with sulphuric acid and the reduction of surface reflection observed. A price list of optical instruments dated 1820 gives information regarding the instruments then manufactured, which included a heliometer, telescopes up to 6 in. aperture and one of 8½ in. in construction, microscopes, achromatic objectives and so on. In 1824 was completed the great Dorpat refractor of 9½ in. aperture, which Fraunhofer considered his masterpiece, and which won for him the freedom of Munich and the civil order of the Bavarian Crown.

In 1824, Fraunhofer became Professor and Conservator of the Physical Section of The Royal Academy, with a yearly stipend of 800 florins. He was then spending most of his time in Munich, only going to Benediktbeuern periodically to supervise the glass manufacture. He seems to have had little time for relaxation, though he was fond of taking walks in the neighbourhood, and his constitution which was never strong, began to show signs of the strain of his efforts. In 1824, signs of tuberculosis appeared and were aggravated by his catching a chill after bathing when overheated. No one appears to have considered the possibility of his early demise, and it was not until almost too late that he chose one, F. A. Pauli, to be instructed in his knowledge and methods. He continued to conduct his affairs from a sick bed, but in June 1826, he could hold out no longer, and passed away at the early age of 39. He was given a State funeral, and buried in Munich. Prior to his death, negotiations were in hand for the taking over of the Optical Institute by the State, but his death put an end to the proposal.

The remaining partner, already an elderly man of 63, was hard put to it to know how to carry on. He had invested large sums in the business and was determined to continue his policy of monopoly. In the meanwhile, however, Guinand's secret was becoming known to others, and opticians were obtaining glass from Guinand himself, and elsewhere. In 1827, the French glassmaker Bontemps purchased the secret from Guinand's son, Henri, and was soon able to master the process and supply the French opticians.

At first Utzschneider undertook the production of glass himself, and the services of Pauli were not made use of for some reason unknown. The conduct of the optical section of the business was entrusted to Georg Merz, who had worked under Fraunhofer since 1808. He was a local man and came as a boy of 15 to help with the furnace work, experience which came in useful later on. Utzschneider started a school for apprentices, which was attended by five boys of whom Merz was one, and instruction was given by an ex-monk, by name Rauch, in mathematics, geometry and chemistry. During the day the apprentices worked at glass polishing, and it is perhaps hardly to be wondered at that Merz was the only one to survive the rigorous training. Utzschneider seems to have been content to continue to make the usual types of glass, and to have made no effort to follow up Fraunhofer's ideas for reducing the secondary spectrum. Towards the end of 1832, the conduct of the glassworks was handed over to Merz, and in 1839 he purchased the business, including the optical section at Munich. Sigmund Merz, Georg's second son, followed his father from 1867 up till 1883, when he gave up in favour of his cousin Jakob Merz, and the glassworks seem to have been abandoned in 1883 or 1884, probably owing to the fact that wood for firing had become increasingly expensive, and owing to competition from other opticians, who were able to obtain glass of better quality than Merz's from France and England.

It may be of interest here to mention Georges Bontemps's call on the firm in 1850 on behalf of Chance Brothers by whom he was then employed. He reported that the Merz firm continued to make glass for their own use only.

Little, if any, technical progress was made, though Georg and his son made attempts to produce pairs of glasses with more equal partial dispersions, but seemingly without success. Jakob Merz continued for some years as head of the optical firm, which specialized in astronomical telescopes, and sold his businesses to Paul Zschokke in 1903. Some two years ago, the old works were sold by the heirs of the Merz family to Prof. Küchler, before mentioned.

I cannot close this account of these works of historic importance without referring once more to the help I have received from the works of Prof. von Rohr and Dr A. Seitz, the author of *Joseph Fraunhofer and his Optical Institute*. Nearly all my facts are due to their researches.

Fraunhofer's early demise can only be described as a tragic loss to science. The advancement of optics would certainly have been more rapid had he survived, and we cannot but regret that his successors had not the ability to pursue the lines of research upon which he was engaged

THE ESTIMATION OF AMETROPIA BY THE COINCIDENCE OPTOMETER

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Received 9 *May* 1937. *Read* 3 *June* 1937

ABSTRACT. 110 cases of refractive error* were examined by means of the Fincham coincidence optometer, and seven had to be rejected as unsuitable. The results in the remaining 103 cases were checked by refraction and subjective testing. The patients were unselected, and a wide range of refractive errors was involved. No cycloplegic was employed on any case. On the assumption that the result obtained by retinoscopy and subjective testing to be correct, the margin of error has been determined and is given. The results compare very favourably, as regards accuracy, with the results of retinoscopy by an expert (the patients' pupils being undilated). Possible sources of error are discussed. Special types of case are discussed: aphakia, amblyopia, and irregular astigmatism. The optometer provides a means of analysing cases of irregular astigmatism accurately. Cases unsuitable for examination by the optometer are, with certain exceptions, found to be cases unsuitable for refraction by retinoscopy without the use of a cycloplegic. The estimation of the corneal astigmatism by keratometry is found not to give an accurate measure of the total astigmatism of the eye as a whole.

§ 1. INTRODUCTION

THE coincidence optometer affords a novel method of estimating errors of refraction. The purpose of the present paper is to describe the results of an investigation made to assess the clinical and research value of the instrument from three points of view. First, its accuracy; second, to compare it, in practice, with the standard method of estimation of refractive errors by retinoscopy and subjective testing; and third, to appraise the value, for research purposes, of the additional facilities it affords in cases of spherical ametropia and astigmatism.

The results discussed here were drawn from the examination of 110 eyes. The patients were hospital patients, chosen more or less at random from the wards; the only criteria employed in their selection being that the eyes chosen should be free from gross disease, and that the ocular media should be reasonably transparent. The ages of the individual patients ranged from 12 to 74 years, and the refractive errors from about +12 to −12 dioptres. Some of the eyes were aphakic, and some were amblyopic; the results of these special cases will be discussed separately under appropriate headings. No mydriatic or cycloplegic was used in any of these cases. Taking into consideration the smallness of the pupils, the irregularity of the refraction, and the lack of co-operation in many of the cases, especially the young or aged patients, it is fair to say that such a series provides a severe clinical test of any method of refraction; and that when examined for control purposes by the routine method of retinoscopy and subjective testing, they presented special difficulties in many cases.

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* A short definition of certain technical terms which appear in this paper may be of use to some readers. *Amblyopia*: a condition in which the sight of an eye is defective although no organic or structural cause sufficient to account for the defect can be identified. A squinting eye is often found to be amblyopic. The causation of amblyopia is uncertain, and is the subject of controversy; in cases of squint the cause probably lies not in the eye itself, but in the cerebral connexions responsible for the interpretation of the visual pictures; these may never have developed properly, or may have become defective from disuse, or there may be an active process of suppression or inhibition. *Mydriatic*: a term applied to drugs which cause dilatation of the pupil. *Cycloplegic*: a term applied to drugs which paralyse the power of accommodation. *Aphakia*: a term employed to denote an eye from which the crystalline lens is absent.

For purpose of comparison, the cases were all examined by the routine method, and as is customary, the strongest plus or weakest minus sphere, and the weakest cylindrical correction was chosen, which would yield the best visual acuity obtainable for the individual eye under examination. The result so obtained was taken as the standard, to represent the static refraction of the eye examined. Certain theoretical objections can be raised against the use of such a standard, but as the purpose of the investigation was to assess the clinical value and accuracy of the coincidence optometer, this seemed to be the most useful and convenient standard to employ.

The cases were also examined by means of the optometer, and the results obtained in this way were then compared with the standard, and classified according to the amount by which they departed from it. It should be understood that in the preparation of the standard result both objective means (retinoscopy) and subjective checking (subjective testing) had been employed; the optometer figures were used directly, without subjective testing. This should be remembered in considering the results, which are tabulated below.

§ 2. ANALYSIS OF RESULTS

Of the 110 eyes examined, seven were found to be unsuitable for various reasons; the ocular media were cloudy, or central fixation was defective, or the pupils were too large or too small to permit accurate readings. For the remaining 103 cases, the results were recorded in duplicate—the values for the upper and lower halves of the pupil. Then selecting the best or mean of these two halves (for reasons to be discussed later), the agreement with the standard values was as follows:

Within 0·25 D. sphere and 0·25 D. cylinder, and 10° axis, 60 cases agreed, and 43 did not.

Within 0·50 D. sphere and 0·50 D. cylinder, and 10° axis, 85 agreed, and 18 did not.

Spherical error

Considering the spherical correction alone:

Within 0·25 D. sphere	... ...	67 cases
Within 0·50 D. sphere	... ...	89 cases

Cylindrical error

Within 0·12 D. cylinder and 10°	59 cases
Within 0·25 D. cylinder and 10°	88 cases
Within 0·50 D. cylinder and 10°	94 cases

Cylinder axis error

Omitting 13 cases where a cylinder was shown by the standard, and not by the optometer, or vice versa, the agreement was as follows:

Complete agreement	65 cases (70%)
Within 0–5°	14 cases (16%)
Within 5–10°	5 cases (5·5%)
Over 10°	6 cases (6·5%)

Thus in 86 per cent of the cases the agreement was within 5°, and in 91 per cent within 10°.

Considering that no cycloplegic was used in these examinations, it is fair to say that the accuracy obtained in these results compares favourably with the standard of accuracy obtained from retinoscopy by an expert. In 90 per cent of the cases the result was correct within 0·50 D. sphere and 0·25 D. cylinder and 10° of axis. The spherical measurement results are not quite so accurate as the cylindrical, because more sources of error are introduced.

The length of time required to make the observation is about the same as would be required for a retinoscopy of a similar degree of accuracy; and it must be remembered that such quickness and accuracy by retinoscopy requires months of practice, whereas the technique of the optometer can be learnt after a few sittings. Except for expert retinoscopists, the result can be obtained more quickly and accurately by the optometer.

§ 3. SPECIAL CASES

(1) *Aphakia.* Aphakic cases present special difficulties. The maximum hypermetropic error which can be recorded by the optometer is + 12 dioptres. This is frequently exceeded in aphakic eyes, especially in the vertical meridian. In order that very high hypermetropic errors can be recorded, a special auxiliary convex lens may be fitted to the optometer, or worn by the patient in a spectacle frame during the examination; the dioptric value of this lens is then added to the result given by the optometer. The distance of the patient from the optometer must be accurately adjusted, or an appreciable error may be introduced, when high errors are being measured. Apart from these technical difficulties, it is often found that the retinal images are poor and indistinct. This may be the result of cloudiness of the ocular media, but more frequently seems to arise from the presence of opaque strands of the posterior lens capsule in the pupil. The patients examined had all been subjected to the extracapsular cataract operation; in this operation the posterior lens capsule

remains intact, and a hole is subsequently cut in it at a further operation, in order to permit the patient to see through it. It is desirable, for various surgical reasons, that this hole should be small; a small hole will permit of good vision with a correcting glass, but when such an eye is examined by the optometer, the small gap in the opaque capsule acts like a small pupil, and the retinal images are indistinct. The results of six cases are appended. It is hoped that at some later date it may be possible to obtain readings from patients where the intracapsular operation has been performed, when the posterior lens capsule would no longer interfere. In aphakia, of course, accommodation, one potential source of error, is abolished.

(2) *Amblyopia.* Amblyopic eyes present special difficulties in that central fixation is often poor or not well maintained, especially where the visual acuity is poor. Nystagmus may be present. The best subjective correcting glass is often a poor guide to the basic refraction of the eye; if the visual acuity is poor, the discriminative power of the patient tends to be poor also. A number of cases were however examined, and certain interesting points arise from consideration of them.

An amblyopic eye usually has a large error of refraction, and some degree of irregular astigmatism is often found to be present in such eyes. Optically, the amblyopic eye is usually the poorer of the two. Some interesting cases were however encountered in which the refraction of the amblyopic eye was quite regular, and the error of refraction small; in some of these cases there seems to be no substantial difference in refraction between the two eyes, and in some rather rare cases, the amblyopic eye seems optically to be the better of the two. This opens up an interesting field for speculation as to why the patient should have elected to employ the eye more optically defective, and allowed the eye which forms the better optical images to become amblyopic.

(3) *Irregular astigmatism.* The optometer provides a ready means of estimating the total refractive error of the eye in any desired meridian, and therefore allows cases of irregular astigmatism to be analysed and studied in detail. Readings can be taken at 10° intervals over the whole circle of the pupil, and the results plotted on a chart. It is surprising how good the visual acuity of an eye may be, in spite of the presence of a considerable degree of irregular astigmatism.

A simple type of irregular astigmatism is found in such a case as No. 17, where there was a corneal nebula occupying a small area of the pupil. The area covered by the nebula presented quite a different refraction from the rest of the pupillary area, and was appreciably more myopic.

In another type of case, a substantial difference in refraction is found, between two halves of the pupillary area; say, upper and lower. In such cases the difference seems to lie in the spherical and cylindrical powers; the axis of the astigmatism is usually the same, unless the whole cornea is grossly irregular.

The best subjective findings in such cases suggest that in some of them the optical image formed by the one half of the pupillary area is utilized (usually that of the better half), and the image of the other half is disregarded. Sometimes the best subjective correction is the mean of the two.

In these investigations one great merit of the coincidence optometer is clearly shown; by no other means is it possible accurately to estimate the astigmatism of an eye in any desired meridian.

(4) *Unsuitable cases.* Certain cases are found to be unsuitable for examination by the optometer. Some of the difficulties are common to other methods of estimation of errors of refraction, such as poor co-operation, low intelligence, poor fixation, nystagmus, opacities on the cornea (mucus, discharge), opacities in the cornea, lens or vitreous. A pupil less than 2½ mm. in diameter is too small to permit the ingress and egress of the beam of light from the optometer, and the optical images are faint and uncertain. A pupil larger than 6 mm. in diameter may be an advantage for retinoscopy, but is a disadvantage in the use of the optometer, since the boundaries of the pupil are no longer visible, and accurate centration is impossible.

Accommodation provides difficulties common to all methods for the estimation of refraction without the use of cycloplegics.

The type of patient in which the greatest difficulty is encountered in securing full relaxation of the accommodation, is the young adult (often of a rather neurotic tendency), and often the low myope, rather than the hypermetrope. This is perhaps rather surprising. Accommodation in itself provides no insuperable obstacle. Provided that the amount of accommodation remains constant during the examination, the amount of the astigmatic error, and the axis of the astigmatism can be accurately determined, and the final result is incorrect only in that it gives too myopic a spherical correction. This is easily discovered and adjusted by subjective testing afterwards.

Fluctuation of the accommodation during the examination, as with retinoscopy, renders the findings wholly unreliable. Fortunately such cases can be identified at an early stage of the examination by the fluctuating positions of the retinal images, which is highly characteristic; and the refraction must be estimated under a cycloplegic.

§ 4. COMPARISON WITH KERATOMETRY

A number of cases were also examined by means of a keratometer, and the corneal astigmatism was measured and recorded.

The keratometer is the only optical instrument commonly used in refraction work, and while it cannot be denied that it is an instrument of precision, in that it measures the corneal astigmatism with a high degree of accuracy, these investigations tend to show that it is fallacious to assume that the corneal astigmatism is the same as the astigmatism of the whole dioptric apparatus of the eye, or even that the two values bear any constant relationship to each other. It is hardly to be anticipated that such a relation would exist.

Nevertheless correction factors have been devised, by means of which it is said to be possible, given the corneal astigmatism, to deduce the astigmatism of the whole eye.

Javal's rule, the best known of these correction systems, was employed for this investigation. Several keratometers were tried, and the most accurate one was eventually employed. Thirty-five eyes were examined in the present series, and the values for the corneal astigmatism corrected by Javal's rule.

In only ten cases (27 per cent) did the corrected values agree with the standard refraction within an experimental error of 0·50 dioptre, and 10° of axis setting. The corresponding figure for estimations by the optometer was over 90 per cent.

§ 5. SOME THEORETICAL CONSIDERATIONS

For practical purposes it was assumed that the standard value employed represented the nearest readily obtainable approach to the true static refraction of the eye. Although perhaps this may be justifiable for experimental purposes, certain theoretical considerations show that an appreciable error may be introduced in assuming that the best correcting glass obtained in this way represents the static refraction of the eye; in fact the very existence of a definite fixed value for the static refraction of a specific eye can hardly be justified on theoretical grounds. The numerous optical defects to which it is known that the dioptric apparatus of the eye is subject, and indeed the very nature of light itself, entail imperfect resolution in the images they form; spherical aberration, diffraction, and the other optical defects produce imperfect resolution of the image, which is itself formed on a receptive layer of finite depth; and if the accommodation has not been paralysed by a cycloplegic, physiological fluctuations in its tone no doubt provide a further source of possible variation. The concept of a static refraction is thus to some extent a contradiction in terms.

Depth of focus provides another possible source of error, and will permit good vision to be obtained even though a hypermetrope is slightly overcorrected, or a myope slightly undercorrected. Again, conventional subjective testing at 6 m. introduces a possible error of one sixth of a dioptre. Finally, as in all methods depending on subjective testing, the accuracy of the standard depends in the last resort upon the discriminate powers of the patient, thus introducing a variable and incalculable personal element. This factor again will introduce a possible source of error in estimating the astigmatism of the eye, where the other factors are less significant.

The clinical findings are found to agree with the theoretical considerations outlined above. To summarise, it may be said that the results obtained from the optometer, without subjective testing, agree very closely with the results obtained by retinoscopy and subjective testing, the agreement being closer for the astigmatic than for the spherical component of the error of refraction; if subjective testing be omitted, the optometer results agree with the basic refraction of the eye more closely than mere retinoscopy, unchecked, unless the retinoscopy is done very expertly indeed.

For practical purposes, it is very much more important to be able to estimate the astigmatism, and its axis, accurately, than to be able to estimate the spherical error accurately; the latter can be checked subjectively so much more easily.

It must therefore be supposed that the basic refraction of the eye is itself probably variable within small physiological limits, and that the subjective standard chosen for our present purpose may again depart from it within a small range of error.

The possible sources in the observations made with the coincidence optometer have been outlined; the main probable sources of error are two:

(*a*) Spherical aberration; the observations may not have been made upon a zone of the pupil which is a fair mean; the optical and visual axes may not coincide.

(*b*) Accommodation: the adjustment of the fixation target may not have succeeded in producing complete relaxation of the accommodation.

It is therefore apparent that as far as the spherical part of the error of refraction is concerned, the basic value is itself liable to an appreciable error; estimation by the optometer is also liable to certain errors; whereas as far as the astigmatic correction is concerned, the basic values are more rigid, and can be more nearly approached. The main source of astigmatic error in the standard is probably the discriminative powers of the patient, and, with the optometer, fluctuation of the accommodation during the examination. It would thus be anticipated that the agreement between the optometer and the standard would be closer as regards cylindrical, than as regards spherical correction; and this is found to be the case. The margin of error is greater when the eye concerned is amblyopic, and subjective testing is therefore more or less unreliable; or where one eye only is accessible for examination, the other being covered; a circumstance which may affect the state of accommodation of the uncovered eye.

§ 6. ACKNOWLEDGMENTS

The author wishes most gladly to acknowledge his indebtedness to the Honorary Staff at Moorfields Eye Hospital for permission to use their patients in making these investigations, and for their unfailing encouragement and kindness at all times; and to Mr E. F. Fincham, for his advice and co-operation, without which this paper could not have been compiled; also to Mr Victor Purvis, for most helpful criticism and suggestions.

Acknowledgment is also due to the instrument maker for the loan of the instruments employed.

Table 1. Tabulated results of the 103 eyes examined

The first column shows the reference number of the case; the second column gives the side to which the eye belonged; the next section shows the standard result for the refraction of the eye, obtained by retinoscopy and subjective testing, and the best visual acuity obtainable with that correction; the final two sections show the corresponding results for the upper and lower halves of the pupil respectively, obtained by the optometer.

No.	Eye	Age	Standard				Optometer					
							Upper half			Lower half		
			Sphere	Cyl.	Axis	Visual acuity	Sphere	Cyl.	Axis	Sphere	Cyl.	Axis
1	L.	14	+4·50	+0·50	45°	6/5 pt	+2·25	+1·75	82°	+3·50	+1·50	85°
2	L.	16	+0·50	—	—	6/5	+1·00	—	—	+1·00	—	—
3	L.	12	−0·50	+0·25	30°	6/9	−0·25	—	—	−0·25	—	—
4	R.	24	−1·25	—	—	6/5	−1·25	—	—	−1·25	—	—
5	R.	32	+4·00	+1·25	75°	6/5	+4·00	+1·00	75°	+4·12	+1·12	75°
6	R.	24	+1·75	—	—	6/5 pt	+1·25	—	—	+1·25	—	—
7	R.	19	+1·50	+1·75	90°	6/5 pt	+1·50	+2·00	95°	+1·50	+2·25	95°
8	R.	15	+3·50	+0·50	145°	6/5	+3·25	+0·75	145°	+3·25	+0·75	145°
9	R.	17	+2·75	+0·25	90°	6/5	+3·25	+0·25	90°	+3·00	+0·25	90°
10	L.	17	+2·50	+0·75	90°	6/5	+3·25	+0·50	100°	+2·75	+1·00	100°
11	R.	31	+2·25	+1·50	20°	6/5	+2·25	+1·50	30°	+2·50	+1·25	30°
12	L.	31	+1·00	+0·25	90°	6/5	+1·00	—	—	+1·00	+0·25	120°
13	R.	39	+0·75	—	—	6/5	+0·50	—	—	+0·50	—	—
14	L.	39	+1·00	+0·25	180°	6/5	+0·50	+0·25	180°	+0·50	+0·50	180°
15	L.	13	+2·00	—	—	6/5	+2·00	—	—	+2·00	—	—
16	R.	25	—	+0·25	90°	6/5	—	+0·25	90°	—	+0·25	90°
17	R.	25	−1·00	+2·25	145°	6/5	−1·50	+2·25	145°	−1·50	+2·25	145°
18	R.	29	+0·50	+0·25	90°	6/6	+0·25	+0·25	90°	+0·25	+0·50	90°
19	R.	25	−2·25	+2·50	95°	6/9	−2·75	+2·75	100°	−2·75	+2·50	100°
20	L.	25	−1·25	+2·25	80°	6/9	−1·25	+2·75	80°	−1·00	+2·50	80°
21	R.	32	+0·50	+0·25	30°	6/6	+0·50	+0·25	30°	−1·25	+2·25	30°
22	L.	32	—	+2·00	60°	6/6 pt	+0·25	+2·75	60°	+0·75	+2·00	60°
23	R.	23	+2·00	+1·00	40°	6/5 pt	+2·75	+0·75	30°	+2·50	+1·25	30°
24	R.	35	+0·25	—	—	6/5	+0·50	—	—	+0·50	—	—
25	R.	15	−1·00	+3·00	170°	6/6	−1·00	+2·25	170°	−0·75	+2·75	170°
26	L.	15	+2·50	+1·50	150°	6/6	+1·25	+2·50	135°	+2·50	+1·00	150°
27	L.	19	+4·00	—	—	6/6	+4·00	—	—	+4·00	—	—
28	L.	19	+2·25	+0·50	160°	6/5	+2·25	+0·50	160°	+2·25	+0·50	160°
29	L.	25	—	+1·50	90°	6/5	—	+1·00	110°	−0·50	+1·50	120°
30	R.	23	+1·50	−4·00	25°	6/6 pt	+1·50	−4·25	25°	+1·75	−5·00	25°
31	R.	14	+1·00	—	—	6/5	+1·25	—	—	+1·25	—	—
32	L.	19	+1·25	+1·00	110°	6/6	+2·00	+1·25	110°	+1·50	+1·00	110°
33	L.	23	+6·00	+0·50	180°	6/6	+5·50	+0·50	165°	+5·50	+0·50	165°
34	R.	24	—	+2·25	155°	6/9	—	+2·25	155°	—	+2·25	155°
35	L.	24	—	+2·00	40°	6/9	—	+1·75	40°	—	+2·25	40°
36	L.	19	−0·50	+1·50	80°	6/9	−0·75	+2·25	70°	−0·50	+2·00	70°
37	L.	25	+0·25	+0·25	90°	6/5	+0·25	+0·25	100°	+0·25	+0·25	95°
38	R.	53	−1·50	−1·00	90°	6/6	−2·00	−1·00	115°	−1·00	−2·00	105°
39	R.	27	+0·50	+1·00	160°	6/5	+0·25	+1·25	105°	+0·25	+1·00	105°
40	L.	27	+0·50	+1·00	100°	6/5	+0·25	+1·25	105°	+0·25	+1·00	105°
41	R.	19	+0·25	—	—	6/5	—	—	—	—	—	—
42	L.	48	+0·25	+0·25	10°	6/5	+0·25	+0·25	10°	+0·25	+0·25	10°
43	R.	16	—	+3·50	100°	6/6 p	+0·25	+3·00	105°	−0·25	+3·25	105°
44	L.	16	−0·50	+1·50	80°	6/5 p	+0·25	+1·25	80°	−0·50	+2·00	80°
45	L.	50	+0·25	+0·25	90°	6/5	+0·25	+0·25	100°	+0·25	+0·25	95°
46	R.	16	+1·75	+0·25	105°	6/5	+1·00	+0·50	105°	+1·00	+0·75	105°
47	L.	16	+1·50	—	—	6/5	+1·75	—	—	+1·75	—	—
48	L.	27	−11·0	−0·75	170°	6/5	−11·75	−1·25	170°	−11·75	−0·75	170°
49	R.	38	—	—	—	6/6	−0·50	—	—	+0·25	−1·25	120°
50	L.	11	+1·75	—	—	6/5	+1·50	—	—	+1·50	—	—
51	R.	24	—	+2·25	155°	6/6 p	−1·25	+2·50	150°	−1·00	+2·50	150°
52	L.	24	—	+2·00	40°	6/6 p	−1·50	+3·00	45°	−1·25	+2·75	45°

Table 1 (*continued*)

No.	Eye	Age	Standard				Optometer					
							Upper half			Lower half		
			Sphere	Cyl.	Axis	Visual acuity	Sphere	Cyl.	Axis	Sphere	Cyl.	Axis
53	R.	62	—	−1·50	110°	6/6	—	−1·50	110°	−0·50	−1·50	110°
54	L.	19	+0·75	—	—	6/5	+0·50	—	—	+0·50	—	—
55	R.	16	+1·00	+3·00	90°	6/9	+1·00	+3·00	90°	+1·00	+2·75	90°
56	L.	16	+4·00	+1·00	100°	6/6	+3·50	+1·25	105°	+3·50	+1·25	105°
57	R.	16	+2·00	+1·75	70°	6/5	+1·50	+1·75	80°	+1·50	+1·50	80°
58	L.	16	+1·25	+3·00	95°	6/5	+1·25	+2·75	95°	+1·25	+3·00	95°
59	R.	27	−1·25	—	—	6/5	−0·25	−0·75	170°	−0·50	—	—
60	L.	27	−1·00	—	—	6/5	+0·25	−0·25	25°	−0·25	—	—
61	R.	34	+0·25	−0·50	180°	6/5	−0·25	−1·25	180°	—	−1·50	180°
62	L.	28	−0·75	+1·00	10°	6/5	−0·75	+1·00	10°	−0·75	+1·00	10°
63	R.	43	—	—	—	6/5	—	+0·25	80°	—	+0·50	80°
64	R.	62	−0·75	—	—	6/5	−0·75	—	—	−0·75	—	—
65	L.	62	−1·25	—	—	6/5	−1·75	—	—	−1·75	—	—
66	R.	54	+0·25	—	—	6/5	+0·75	—	—	+0·75	—	—
67	L.	41	—	+1·00	140°	6/9	−0·50	+1·75	135°	+0·25	+1·00	150°
68	R.	21	+1·25	+4·00	80°	6/5	−0·25	+4·75	75°	+0·25	+4·50	75°
69	L.	43	+0·25	+0·50	120°	6/5	+0·25	—	—	+0·25	—	—
70	R.	9	+0·25	+0·75	90°	6/5	+0·25	+0·25	85°	−0·25	+0·25	85°
71	L.	9	+0·25	+0·25	90°	6/5	−0·25	—	—	−0·25	—	—
72	R.	57	+1·50	+0·50	50°	6/5	+1·25	+1·00	50°	+1·50	+0·50	50°
73	L.	14	+3·00	—	—	6/5	+0·50	—	—	+0·50	—	—
74	R.	21	+0·25	—	—	6/5	—	—	—	—	—	—
75	R.	67	+2·00	—	—	6/6 pt	+2·00	+0·75	80°	+2·00	+0·75	80°
76	L.	43	+0·75	+0·50	180°	6/5	+1·00	—	—	+1·00	—	—
77	R.	49	−0·25	+0·25	180°	6/5	—	—	—	—	—	—
78	L.	24	+0·25	−0·75	175°	6/5	+0·25	−0·75	175°	+0·25	−1·00	175°
79	R.	44	—	—	—	6/6	−0·50	—	—	−0·50	—	—
80	L.	44	−0·50	—	—	6/6	−1·00	—	—	−1·00	—	—
81	L.	20	—	+0·25	180°	6/5	−1·50	−0·50	105°	−1·75	−0·50	105°
82	R.	30	+0·75	—	—	6/5	+0·50	+0·25	155°	+0·50	+0·25	155°
83	L.	33	−0·25	—	—	6/5	—	—	—	—	—	—
84	R.	57	+0·25	+0·25	180°	6/5	+0·50	—	—	+0·50	—	—
85	R.	27	+0·25	−1·25	20°	6/5	+0·25	−1·50	20°	+0·25	−1·00	20°
86	L.	52	—	−0·25	180°	6/5	−0·25	—	—	+0·25	—	—
87	R.	28	−0·25	+0·75	40°	6/5	−0·25	+0·75	40°	—	+0·50	40°
88	L.	45	+1·00	−0·25	180°	6/5	+1·50	—	—	+1·25	+0·25	180°
89	R.	20	+0·25	—	—	6/5	−0·25	−0·25	90°	−1·00	−0·50	100°
90	L.	17	+3·00	+0·25	95°	6/5	+3·75	+0·75	95°	+4·00	+0·25	95°
91	L.	36	+1·00	+1·75	5°	6/6 pt	—	+1·50	5°	—	+1·50	5°
92	R.	41	−1·25	—	—	6/6	−2·25	—	—	−2·25	—	—
93	L.	41	−1·75	—	—	6/9	−2·75	—	—	−2·75	—	—
94	R.	36	−0·25	−0·75	110°	6/6	−0·50	−0·50	110°	−0·50	−0·25	110°
95	L.	44	−2·00	−0·50	175°	6/5	−2·00	−1·00	175°	−2·50	−0·25	175°
96	R.	42	−0·75	+1·50	85°	6/6	−1·00	+2·00	90°	−0·50	+1·75	85°
97	L.	42	−0·25	+1·50	75°	6/6	−0·75	+2·50	75°	—	+1·50	75°
98	L.	52	−0·50	+0·25	120°	6/5	−0·50	—	—	+0·50	−0·50	35°
99	L.	50	+0·50	+0·50	150°	6/5	+0·25	+0·75	150°	+0·50	+0·75	150°
100	L.	42	+0·50	+0·25	55°	6/5	+0·25	+0·50	55°	+0·75	+0·75	145°
101	R.	26	+2·50	+1·75	45°	6/9 pt	+2·50	+2·00	55°	+2·50	+2·00	50°
102	R.	49	−2·25	—	—	6/5	−2·25	—	—	−2·25	—	—
103	L.	49	−2·00	−0·25	180°	6/5	−2·25	—	—	−2·25	—	—

Table 2. Aphakic cases

This table is an appendix to table 1, dealing with six aphakic cases. The arrangement is the same as in table 1.

No.	Eye	Age	Standard				Optometer					
							Upper half			Lower half		
			Sphere	Cyl.	Axis	Visual acuity	Sphere	Cyl.	Axis	Sphere	Cyl.	Axis
1	R.	50	−3·00	+9·00	160°	6/12	−2·75	+11·00	160°	—	—	—
2	R.	44	+0·50	+4·50	5°	6/5	+0·75	+4·25	5°	+0·75	+4·25	5°
3	L.	74	+12·00	+1·50	180°	6/9	+11·75	+1·00	175°	+11·25	+1·50	180°
4	R.	45	+9·00	+3·50	180°	6/18	+8·25	+3·50	170°	—	—	—
5	L.	45	+7·00	+2·50	180°	6/9	+6·25	+2·75	25°	+6·75	+2·75	180°
6	R.	60	+12·00	+2·00	20°	6/9	+11·25	+0·75	25°	+10·75	+1·00	30°

Table 3. Amblyopic cases

This table deals with eighteen amblyopic cases; the arrangement is as in tables 1 and 2.

No.	Eye	Age	Standard				Optometer					
							Upper half			Lower half		
			Sphere	Cyl.	Axis	Visual acuity	Sphere	Cyl.	Axis	Sphere	Cyl.	Axis
1	R.	14	+5·00	—	—	6/24	+5·00	—	—	+4·50	+1·00	115°
2	R.	16	+0·50	—	—	6/24	+0·75	+0·25	75°	+0·75	+0·50	80°
3	R.	12	−6·50	−1·25	150°	c.f.	−6·00	−2·75	160°	−6·00	−2·00	70°
4	L.	32	+5·00	+1·50	80°	6/18	+5·25	+1·25	90°	+5·00	+1·25	90°
5	L.	24	+2·75	+1·75	75°	6/24	+2·00	+2·00	75°	+2·75	+0·75	75°
6	L.	19	+1·75	+2·75	100°	6/18	+1·75	+3·00	90°	+2·00	+2·75	90°
7	L.	15	+0·75	+1·75	135°	c.f.	+0·75	+2·25	135°	+1·00	+1·50	130°
8	R.	13	+2·00	—	—	3/60	+2·25	—	—	+2·25	—	—
9	L.	29	+0·25	+1·25	60°	6/12	−0·50	+1·25	50°	−0·50	+1·25	55°
10	L.	23	+2·50	+1·50	160°	6/50	+4·50	+1·25	150°	+4·75	+1·25	150°
11	L.	35	—	+3·00	90°	6/24	—	+3·37	90°	—	+3·25	90°
12	R.	19	+5·25	—	—	6/12	+5·25	—	—	+5·25	—	—
13	R.	19	+2·25	+1·00	60°	6/9	+2·25	+1·00	60°	+2·00	+1·25	60°
14	L.	14	—	−1·50	165°	6/9	+0·25	−0·75	165°	+0·50	−1·25	170°
15	R.	19	+0·25	+5·00	110°	6/24	+0·50	+5·00	110°	+0·50	+4·50	110°
16	R.	23	+6·00	+0·75	120°	6/12	+6·25	+0·75	110°	+6·00	+0·75	105°
17	R.	17	+3·00	+1·25	45°	6/9	+4·00	+1·25	45°	+4·25	+0·50	45°
18	L.	26	+4·00	—	—	6/18	+4·25	—	—	+4·25	—	—

Table 4. Comparison of the keratometer and the optometer

This table shows the compared results in 33 cases examined with the optometer and the keratometer. Cylinder values alone are given.

The first column shows the number of the case; the second column gives the cross reference number (see table 1); the next section gives the standard cylinder value; the next two sections give the cylinder values as given by the optometer for the upper and lower halves of the pupil; and the last section gives the corrected keratometer reading, using Javal's rule.

No.	Ref.	Standard		Optometer				Corrected keratometer readings	
				Upper half		Lower half			
		Cyl.	Axis	Cyl.	Axis	Cyl.	Axis	Cyl.	Axis
1	41	—	—	—	—	—	—	+0·50	180°
2	42	+0·25	10°	+0·25	10°	+0·25	10°	+0·50	180°
3	43	+3·50	100°	+3·00	105°	+3·25	105°	+4·25	100°
4	44	+1·50	80°	+1·25	80°	+2·00	80°	+2·75	80°
5	46	+0·25	105°	+0·50	105°	+0·75	105°	+1·75	180°
6	47	—	—	—	—	—	—	+1·00	180°
7	48	−0·75	170°	−1·25	170°	−0·75	170°	+0·50	80°
8	50	—	—	—	—	—	—	—	—
9	51	+2·25	155°	+2·50	150°	+2·50	150°	+0·75	40°
10	52	+2·00	40°	+3·00	45°	+2·75	45°	+2·50	140°
11	53	−1·50	110°	−1·50	110°	−1·50	110°	+1·25	5°
12	54	—	—	—	—	—	—	+1·75	115°
13	59	—	—	+0·75	170°	—	—	+0·50	90°
14	60	—	—	−0·25	25°	—	—	+0·75	60°
15	61	−0·50	180°	−1·25	180°	−1·50	180°	+1·00	105°
16	62	+1·00	10°	+1·00	10°	+1·00	10°	+1·00	145°
17	63	—	—	+0·25	80°	−0·50	80°	+0·75	100°
18	64	—	—	—	—	—	—	+0·75	90°
19	65	—	—	—	—	—	—	+2·25	95°
20	66	—	—	—	—	—	—	+0·25	105°
21	67	+1·00	140°	+1·75	135°	+1·00	150°	+1·50	45°
22	69	+0·50	120°	—	—	—	—	+1·00	90°
23	70	+0·75	90°	+0·25	85°	+0·25	85°	+1·75	95°
24	71	+0·25	90°	—	—	—	—	+0·50	100°
25	72	+0·50	50°	+1·00	50°	+0·50	50°	+1·50	80°
26	74	—	—	—	—	—	—	+0·50	180°
27	75	—	—	+0·75	80°	+0·75	80°	+0·75	85°
28	76	+0·50	180°	—	—	—	—	+1·00	120°
29	77	+0·25	180°	—	—	—	—	+1·00	125°
30	78	−0·75	175°	−0·75	175°	−1·00	175°	+0·75	85°
31	98	+0·25	120°	—	—	+0·50	125°	+1·25	95°
32	99	+0·50	150°	+0·75	150°	+0·75	150°	+0·25	90°
33	100	+0·25	55°	+0·50	55°	+0·75	145°	+0·50	5°

Table 5. Comparison of the keratometer and the optometer. Aphakic cases

This table is an appendix to table 4, dealing with aphakic cases. The arrangement is the same as in table 4.

No.	Standard		Optometer				Corrected keratometer readings	
			Upper half		Lower half			
	Cyl.	Axis	Cyl.	Axis	Cyl.	Axis	Cyl.	Axis
1	+9·00	160°	+11·00	160°	No readings		+12·00	160°
2	+4·50	5°	+4·25	5°	+4·25	5°	+4·50	5°
3	+1·50	180°	+1·00	175°	+1·50	180°	+2·00	170°
4	+2·50	180°	+2·75	25°	+2·75	25°	+2·50	160°
5	+2·00	70°	+0·75	25°	+1·00	30°	+2·75	25°

DISCUSSION

Mr J. **Adamson**. In dealing with amblyopic cases in connexion with squint treatment I have found that the use of the coincidence optometer has in all cases led me to obtain the best refractive correction. Very satisfactory results have been obtained in cases with irregular astigmatism. Further, I should like to say that in quite a number of cases the optometer result showed a higher cylinder power than the retinoscopy result. In all such cases the optometer finding gave the subject a higher acuity than the retinoscopy finding. This has happened sufficiently frequently to make me wonder whether the cylinder determination by retinoscopy is as reliable as we have always assumed and it seems to me that it is a point which could well be investigated over a larger number of cases.

Author's reply. I am glad Mr Adamson has raised this question. I quite agree that a large proportion of amblyopic eyes show a high degree of astigmatism, not infrequently irregular; and that an examination by the optometer often leads, I think, to a more accurate correction of the refractive error, and an apparent increase in the visual acuity. With regard to the suggestion that the optometer reveals a higher degree of astigmatism, in many cases, than retinoscopy does, I can only say that with the limited data I have tabulated in table 3, this has not been my experience; but I have not sufficient material to justify me in expressing any definite opinion. I am glad the point has been raised however, because this same lack of evidence prevented me from laying any stress on the amblyopic cases in my paper; yet I do feel that it is in the examination of these very cases that the optometer shows itself at the greatest advantage, when compared with retinoscopy. Without the use of a cycloplegic, retinoscopy on an amblyopic eye is difficult; central fixation is poor, and the eye tends to rove about, producing conflicting results; central vision is defective, and in the effort to maintain fixation, the accommodation is apt to fluctuate. I am sure that retinoscopy on an amblyopic eye is not as a rule so accurate as on a normal eye, other things being equal. The optometer is at an advantage. Centration can be frequently and accurately checked; fluctuation of the accommodation can readily be detected by wavering of the images; and I am sure the optometer never shows to better advantage than with such a case. In my paper I have laid no emphasis on this point, which appears to me a very important one, because I had so little evidence, and because I feel that there may be a fallacy in the apparent increase in visual acuity usually obtained. Any prolonged examination and testing of an amblyopic eye tends to show a progressive increase in visual acuity, up to a point, due I believe, to the persevering attention of the patient; but I doubt if much significance can be attached to it, or if it is maintained. Often such a patient will volunteer the information that "the sight comes and goes"; and it is nearly always possible to persuade him slowly to read another line of the test type. Hence I am loath to place much reliance on the increase in visual acuity alone. With these reservations, my experience has been in agreement with that of Mr Adamson, and I agree with him that the investigation of these amblyopic cases is most interesting and, I think, likely to be most profitable.

THE COINCIDENCE OPTOMETER

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Received 2 May 1937. Read 3 June 1937

ABSTRACT. The power of the required spectacle lens may be determined objectively by the ophthalmoscopic observation of the retinal image of a target, the position of which can be adjusted relative to an optometer lens to bring it to the conjugate of the retina. In the past the method has depended upon the observer's estimation of focus, or of parallax between the retinal image and the target which is in the field of the observing system, or of coincidence between the retinal image and an index line in the observing system. This paper describes the principle of an instrument in which the adjustments for both refraction measurement and meridian location of an astigmatic eye are made by a coincidence setting between two parts of the retinal image. By this means the sensitivity of the method is increased by more than 100 per cent.

§ 1. INTRODUCTION

THE measurement of errors of refraction of the eye may be made either by a subjective test, in which the co-operation of the patient is required in describing the effects of the trial lenses, or by an objective method in which the examiner treats the eye purely as an optical system and endeavours to find the power of the lens required to bring the conjugate of the retina to infinity. Undoubtedly in all cases where the visual acuity is good enough the correction found by objective methods must be confirmed subjectively before the prescription is given; the complexity of the visual mechanism may make the true optical correction undesirable. On the other hand, this complexity may introduce difficulties if reliance is placed upon a subjective test alone. Although defects of the optical part of the visual mechanism can be corrected by lenses, the subjective response to the lenses may be influenced by the physiological and mental parts of the mechanism to such an extent that the true optical condition is obscured. It frequently happens that cases with low astigmatic errors are unable to appreciate the effect of the weak cylindrical lenses which would correct the error, although they may be suffering some strain as a result of the defect. Similarly, it is often impossible by subjective tests to find the true correction of an eye with a high refractive error owing to the low visual acuity in one who has never had a sharply focused retinal image. The correction of an amblyopic eye must also call for the employment of an objective test.

The obvious desirability of a method by which the basic refraction of the eye could be determined independently of the subjective interpretation of the retinal and mental image led to the development of objective methods. Retinoscopy has proved the most valuable of these methods, but owing to the variability of the appearances which it gives in different eyes, its employment calls for a considerable degree of experience and skill on the part of the examiner. For this reason some attention has been given in the past to the design of instruments in which the aim has been to measure refraction by the adjustment required to observe objectively a sharply focused retinal image.

§ 2. HISTORY

The objective optometer in its simplest form consists of the combination of the far-point rule with the direct ophthalmoscope. In such an instrument a suitably illuminated target is movable along the rule with regard to the optometer lens; the light after passing the lens is brought into the patient's eye by means of a perforated or transparent mirror, and the examiner looking through the mirror sees the image of the target upon the patient's retina. The refraction is measured by determining the distance from the lens at which the target has to be placed to produce a sharply focused retinal image. In order that the light from the retinal image emerging from the ametropic eye shall focus upon the retina of the observer's eye correcting lenses must be placed in the sight-hole of the mirror.

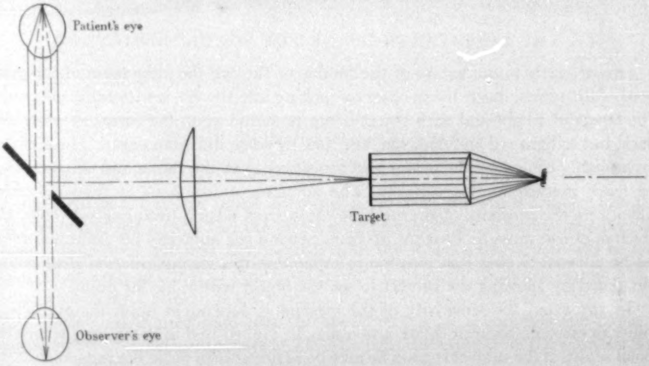

Figure 1. The stigmatometer (Hardy).

The earliest form of this instrument was probably the Hardy Stigmatometer (figure 1). In this the target was caused to move along the rule by a rack mechanism which caused the appropriate correcting lens to be brought before the observer's eye. The principal meridians of an astigmatic eye were determined by the use of targets consisting of radial lines or blocks of lines which could be rotated into different meridians. A separate small target attached to the plate carrying the main target was provided for the patient's fixation. This was set farther away from the optometer lens than the main target in order to induce the eye to relax accommodation, but as it moved with the main target it probably did not achieve its object, especially in astigmatism when the target distance had to be changed in the measurement of the different meridians of the eye.

Later instruments on a similar principle were produced under the name of the Astron Refractometer and the Rodenstock Refractometer. In the last of these a telescopic viewing system was provided to assist the observation of the retinal image.

A difficulty in this type of instrument which employs the direct method of observation is the elimination of the corneal reflexion, as the separation between the illuminating and observing beams which is necessary for the reflex-free condition cannot be achieved. If the usual indirect method for the elimination of reflexions is used, in which the beams are separated by the production of an image of the source of light and of the observing pupil in separate regions of the patient's pupil, a great depth of focus of the target image upon the retina results; thus the required sensitivity is lost.

In an instrument designed by Thorner and manufactured by Busch, the reflex-free condition has been achieved, and by employing almost the full diameter of the pupil for both illuminating and observing systems the maximum sensitivity of the focusing method has been retained.

§ 3. THE DISADVANTAGES OF THE FOCUSING METHOD

Owing partly to the nature of the fundus of the eye the judgement of the exact focus of the retinal image by an observer looking into the eye is somewhat uncertain. The image of a light and dark object is not rendered upon the retina as white and black, but as light red and dark red, and usually some diffusion exists. These effects are probably caused by the colour and translucency of the retina and choroid; they are more marked in fair subjects. The adjustment for focus is rendered more difficult by the necessity of approaching the correct setting from one side only; the effective object must be brought up from beyond the subject's far point and must not be allowed to pass that position in order that the accommodation shall not be stimulated by allowing the subject to see the object within his far point.

In any event the sensitivity of the method is dependent upon the examiner's ability to estimate accurate focus, and it may be argued that in those cases where the visual acuity of the subject is good he may be better able to make the judgement than the examiner viewing his retinal image.

§ 4. THE PARALLAX REFRACTIONOMETER (HENKER)

In this instrument, which is based upon the simplified Gullstrand ophthalmoscope, a new principle which avoids the necessity for the estimation of the sharpness of the retinal image has been introduced in an instrument made by Zeiss.

In the parallax refractionometer the fundamental condition for reflex-free ophthalmoscopy by the indirect method is used. In figure 2 it will be seen that the source of light *S* which is displaced from the axis of the instrument is imaged by the ophthalmoscope lens in a decentred part of the subject's pupil at *S'*, while the pupil of the observing system *P* is imaged in the subject's pupil at *P′*. Thus, whereas the light enters the eye through the area *S′*, only that which leaves through *P′* can enter the observing system. Reflexions from the surfaces of the eye are thus avoided.

A transparent target *T* bearing a vertical index line perpendicular to the plane containing the centres of the areas *P′* and *S′* is placed upon the axis at the principal focus of the lens, and thus its image will be formed upon the retina of an emmetropic eye again upon the axis at *T′e*. If the eye is hypermetropic the light will not reach the axis, and a somewhat out-of-focus retinal image will be formed displaced from the axis; if the eye were myopic the light would have crossed the axis before reaching the retina. By moving the target along the axis of the instrument, away from the lens for hypermetropia and towards it for myopia, the retinal image will be sharply focused and will fall upon the axis when the target is brought to a position which is conjugate with the subject's retina.

In figure 2 the displacement of the retinal image in an emmetropic eye caused by the movement of the target is shown at *T′m* and *T′h*.

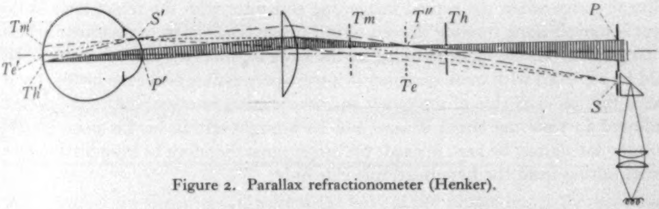

Figure 2. Parallax refractionometer (Henker).

The light of the retinal image emerging again from the eye is reimaged by the eye system and the lens; when the target is conjugate with the retina the emergent image will lie upon the axis and coincide with the target, otherwise it will be displaced to one side or other of the target according to the refractive condition of the eye relative to the position of the target.

In figure 2 it is presumed that the eye is emmetropic and that the target is positioned for a hypermetropic eye at *Th*. The light emerging from the retinal image is reimaged at *T″* displaced from the axis.

The target consists essentially of a glass plate bearing four windows, upon each of which a fine line is ruled. For the measurement of refraction the line of the target is perpendicular to the plane containing the centres of the two areas *S′* and *P′*. This target will be seen by the examiner through the observing system; the line will appear black upon the red background of the fundus which is visible through the window. When the target is not conjugate to the retina the displaced retinal image of the line will appear as a dull red line to one side or other of the black target line. When the target is correctly positioned for the refraction of the eye under test the retinal image will coincide with the target line and will be invisible. The slide along which the target travels is scaled to read the refraction of the eye in dioptres.

For the determination of the principal meridians of an astigmatic eye, target lines are provided which lie in the same plane as the centres of the areas S' and P'. In errors of refraction, the images of these lines will be displaced only in the direction of their length. When the lines do not lie in one of the principal meridians of an astigmatic eye the retinal image will suffer an oblique displacement, which will cause a lack of coincidence to appear between the "meridian lines" of the target and the images of them upon the retina. The principal meridians of the eye are located by rotating the instrument about the axis of the system until coincidence of these lines and their images is obtained.

In principle this instrument appears to have advantages over the focusing types. The smallness of the area through which the light enters the eye ensures considerable depth of focus in the retinal image, and its displacement relative to the target should be easily seen. The sensitivity of the method will depend upon the separation between the centre of the area through which the light enters the eye and the centre of the image of the aperture of the observing system at the subject's pupil, i.e. the distance $S'P'$ (figure 2). In practice the sensitivity depends also upon the operator's ability to judge when the retinal image line coincides with the target line; as the target is moved along its slide the red retinal image line is seen to disappear behind the target line. Its complete masking by the latter signifies the correct setting. This could be achieved with more certainty if it were permissible to let the image appear successively on each side of the target and take a mean position, but as the subject is allowed to view the target it must not be brought within his far-point so that accommodation may be kept relaxed; the target must therefore be brought up to the correct setting from the hypermetropic side only.

§ 5. THE COINCIDENCE OPTOMETER

In the type of instrument that we are considering the chief requirement is sensitivity; the correction of refractive errors is now required to an accuracy of 0·25 dioptre, and the meridians of an astigmatic eye must be known to within a few degrees. In the optometer of the focusing type an error of 0·25 dioptre will cause little apparent difference in the definition of the retinal image; in the parallax type of instrument, the shift of the image across the retina, the effect by which the instrument operates, must depend upon the displacement of the area of the pupil through which the light enters the eye from the centre of the area through which observation is made. If we assume that when working centrally upon an eye with a 3 mm. pupil, this distance can be 1·5 mm., the shift of the retinal image for an error of refraction of 0·25 dioptre will be about 0·007 mm.

If we adopt the general principle of this instrument it is obvious that as the displacement of the retinal image cannot be increased for a given separation between the illuminating and observing beams, and as this is governed by the diameter of the pupil, enhancement in the sensitivity of the method can be produced only by an improvement in the method of observing the displacement of the image. In the parallax method the image becomes hidden by the target at the moment of making the setting; if the position of the image could be observed relative to an index mark which did not hide it, so that a coincidence setting could be made the adjustment would be facilitated. To produce this condition the actual target must not appear in the field of the observing system. Its place may be taken by an aerial image of the target, the light forming it being brought on to the axis of the optometer lens by means of an excentrically placed or transparent mirror which does not interfere with observation.

Another method, the one which was used in the original model of the coincidence optometer, is to separate the image-forming and observing systems, providing an optometer lens for each, and to bring the light into the eye through a decentred area of the pupil by reflexions, so that the virtual position of the target is again upon the axis of the observing system. This method is shown in the diagram (figure 3). The comparison of the position of the image with an index mark is, however, not an ideal method, as the impossibility of matching the appearance of a graticle with the retinal image must reduce the accuracy with which a coincidence alignment can be made.

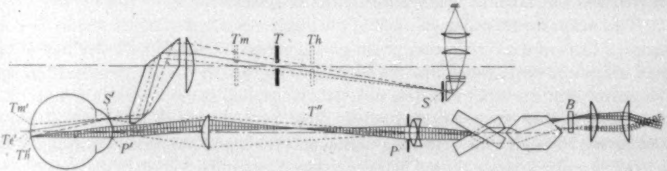

Figure 3. Coincidence optometer.

But provided we obtain an uninterrupted view of the retinal image by using for its "object" an image of the target, we have available a more sensitive method of detecting its displacement than by comparing it with an index mark. Let us suppose that the image whose displacement we wish to detect consists of a single vertical line which lies across the axis of the system when the target is conjugate with the retina, and becomes displaced in a direction perpendicular to its length to the right or left according as the eye is myopic or hypermetropic relative to the position of the target. If now we bisect the field of observation into upper and lower halves and reverse one-half right for left, the effect of displacement of the line will be doubled, the two parts of the line will move at equal rates in opposite directions as the adjustment is made and the setting will consist of bringing the two parts together into coincidence when the image of the target is brought on to the axis of the system.

This is the basic principle of the coincidence optometer. By its adoption we obtain a geometrical increase in the sensitivity of the method of 100 per cent for a given separation between the illuminating and observing beams, i.e. for a given diameter of pupil, in addition to the increased facility of alignment provided by two exactly matched parts of the line. A diagram of the original arrangement of the system is given in figure 3. In this the illuminating system is parallel to the observing system, the light is brought into the eye by means of the rhomboid prism and enters through the decentred area *S′* the image of the effective source *S*. The aperture of the observing system *P* is imaged in the patient's pupil at *P′*. The target *T* consists of a single line, perpendicular to the plane of the drawing, across an aperture; it is movable along the axis of the lens, towards the lens for myopia and away from it for hypermetropia. The target shown in full line is in its normal position, i.e. at the principal focus of the optometer lens; light from it will enter the eye through the area *S′* as a narrow beam parallel to the axis of the observing system, and the target will be imaged upon the axis at *Te′* if the eye be emmetropic.

In the case which is shown we shall consider the target to be placed beyond the principal focus of the lens at *Th*, a position which it would have to occupy to bring the retinal image on to the axis in the case of a certain amount of hypermetropia. In the emmetropic eye which is shown the somewhat out-of-focus retinal image of the target in this position will be displaced from the axis at *Th′*. The light from this image emerging again from the pupil is brought to a focus by the lens of the observing system again off the axis at *T″* and is observed by means of a low-powered microscope which contains the image-dividing system.

The means for reversing one-half of the image relative to the other consists in its simplest form of a 90° reflecting prism placed across the upper or lower half of the field before the eyepiece, so that the beam forming half of the image passes through the prism while the other half does not. In the original model of the instrument the beam was divided into upper and lower halves by tilted parallel plates. The upper part passed through a 90° reflecting prism, and the lower part passed through what is in effect a tilted parallel-sided block, produced by cementing on to the hypotenuse of the reflecting prism another 90° prism of half its height. It was arranged that the two parts of the image were formed upon a thin biprism *B*, the purpose of which was to eliminate the somewhat diffused central part of the image and produce a clean division of the field. The biprism was in the focal plane of the eyepiece. The slide upon which the target moved was scaled to read the refraction of the eye in dioptres.

§ 6. THE DETERMINATION OF THE PRINCIPAL MERIDIANS OF AN ASTIGMATIC EYE

The principal meridians of an astigmatic eye could be located by rotating the apparatus which has been described about the axis of the eye, and by making consecutive measurements the meridians of greatest and least power could be found. Such a method is rather tedious and is not very sensitive; in low amounts of astigmatism the power changes slowly and precise settings are not possible. The method which has been adopted depends upon the displacement of the image in a direction oblique to the plane containing the centres of the illuminating and observing beams when that plane does not coincide with one of the principal meridians of the eye.

We have seen that errors of refraction will cause the retinal image to be displaced in the plane of the illuminating and observing beams, and that such a displacement becomes obvious if the image consists of a line perpendicular to this plane, particularly if the coincidence method of determining its position is used. A line parallel to this plane, however, will be displaced in the direction of its length when an error of refraction is present, and in an oblique direction when the plane of the illuminating and observing beams is not in one of the principal meridians of the eye. In order to detect this displacement due to the obliquity of the principal meridians relative to the plane of the instrument, it is necessary to provide a line in the target perpendicular to the refraction-measuring line, or to rotate the refraction-measuring line through 90°, and also to rotate the image-dividing device in the observing system through 90° so that it will operate upon the line image in its new position.

With the instrument so adjusted errors of refraction will cause no lack of coincidence in the parts of the image because the image will suffer no displacement in the direction in which reversal occurs, but if the eye be astigmatic and the plane of the instrument does not lie in one of the principal meridians, the oblique displacement of the retinal image will become apparent as a lack of coincidence in the two parts of the image seen in the observing system. By rotating the whole system about the axis of the eye the principal meridians can thus be located as the positions in which coincidence occurs, and then by changing back to the refraction-measuring position of the target and image-dividing system, the refraction in each of these meridians may be measured.

In the instrument which has been developed by Messrs Taylor, Taylor and Hobson, and which is described in the paper by Mr Reason, the determination of principal meridians is greatly facilitated by two important improvements in the design. The meridian-location condition is arrived at from the refraction-measuring condition by rotating the effective source of light through 90° about the observing axis; thus, while the target line and the image-dividing system are kept in their original positions the plane of the centres of the illuminating and observing areas is rotated into the direction of the target line. In addition, instead of rotating the whole instrument in order to locate and measure the principal meridians, which is usual with instruments of this type and in keratometers, in the new instrument the image of the pupil formed within the instrument is caused to rotate by the rotation of a reflecting prism. The result of these modifications is that for both refraction measurement and meridian location the observer sees a vertical line image which remains vertical throughout the test whatever meridians of the eye are being tested. The effect of rotating the reflecting prism is to rotate the image of the pupil through twice the angle, and thus the instrument will conveniently operate over the whole 360° of the pupil. This is a valuable asset, as although in a symmetrical eye it is necessary to measure only one-half of the pupil, the detection and measurement of irregular refraction can be made only by a study of all parts of the pupil area.

§ 7. THE SENSITIVITY OF THE METHOD

For an objective method of the determination of refraction to be successful it should be sensitive to differences at least as small as those which can be detected subjectively by a patient with good visual acuity. The sensitivity of the coincidence optometer operating upon an eye can be appreciated from figure 4. This is a photograph of the retinal image in a human eye taken through the optometer. It is reproduced to show the size as it appears to the observer using the instrument and shows the lack of coincidence which occurs between the two parts of the line in an error of 0·5 dioptre. Allowing for some loss of definition in the photography and reproduction it will be seen that a quarter of this error could be detected.

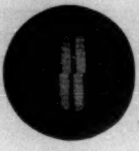

Figure 4. The image on the human retina, photographed through the coincidence optometer. Error of refraction 0·50 dioptre.

Theoretically the sensitivity of the method depends upon the separation between the centres of the illuminating beam and the observing beam in the plane of the pupil (pupil radius), the magnification of the observing system and finally the coincidence acuity of the observer. Assuming a coincidence acuity of 10 sec. (the apparent displacement of the image before it is divided will be half this) and taking the magnification of the system as 1·17, for a pupil radius of only 1 mm. the smallest detectable change in refraction will be about 1/50 dioptre.

An exact test of the sensitivity cannot be made on a living eye owing to small irregularities of refraction which are always present and the possibility of small changes in power due to movement of the patient and to accommodation. I have, therefore, used a model eye constructed of a well-corrected 2-in. microscope objective and a flat metal plate to represent the retina; in the test the optometer adjustment was not altered, settings were made by adjusting the distance of the retina from the lens by means of a divided micrometer screw, until apparent coincidence was obtained in the optometer image. In each test twenty settings were made by an observer with good coincidence acuity. With the minimum pupil radius allowed by the instrument of 1·1 mm., the greatest difference from the mean was 0·016 dioptre. With a pupil radius of 1·5 mm. the greatest difference from the mean was 0·012 dioptre.

The sensitivity of the instrument in the location of a principal meridian of an astigmatic system was also tested. In this case the same model eye was used, its length was kept fixed and a cylindrical trial case lens was mounted in the spectacle plane in a rotating holder. Attached to the lens was a long pointer reading upon a protractor. The optometer, set for meridian location, was kept fixed; settings were made by rotating the cylinder lens until apparent coincidence of the image in the optometer was obtained. Tests were made with a pupil radius of 1·5 mm. The greatest difference from the mean of twenty settings on a 1 dioptre cylinder was 20 min. The greatest difference from the mean of twenty settings on a 0·25 dioptre was $1\frac{1}{2}°$.

This high sensitivity provided by the instrument as it is commercially produced can never be fully reached in working on a human eye, although it will probably be above the differences that can be detected subjectively. The quality of the human retinal image is not so good as that produced by the model eye. This appears to be due to the low optical quality of the eye and to a certain diffusion of light in the substance of the retina or in those tissues which constitute the receiving screen. However, our ability to make an accurate setting by the coincidence method is less affected by diffusion of the image than it is when other methods such as focusing are used.

§ 8. THE CONTROL OF ACCOMMODATION

The measurement of astigmatism of the eye is impossible by any method unless the accommodation is fixed; the measurement of the far-point refraction calls for the complete relaxation of accommodation. In order to achieve relaxation or even fixation of the accommodation, the patient must not be allowed to look at the target of the optometer, because as this is moved towards and away from the eye in the measurement of the various meridians it will cause a variation in the state of accommodation, if it is followed by the patient.

In the coincidence optometer a separate fixation target is provided. It consists of a small aperture in a disk situated in an auxiliary illuminating system. The light from this target is brought on to the axis of the optometer lens by reflexion and thus enters the eye with the light from the main target. The fixation target is separately adjustable and in the usual test is placed as far away from the optometer lens as will permit the patient to see it clearly, i.e. at the equivalent of his far point. The necessary displacement of the measuring target from the fixation target means that the refraction will not be measured at the fovea; the displacement is found to be well within the range over which the refraction is constant.

Another device has been employed to assist in relaxing the accommodation. It is well known that there is a tendency for the eyes to accommodate when looking into a monocular instrument when the eye not in use is occluded. If the optometer is used in a darkened room the effect will be the same as occluding the eye which is not being tested. On the other hand, if the room is not dark there will be a tendency for that eye to look at near parts of the instrument. To overcome these difficulties we present a field of uniform low illumination to the eye by placing before it an opal glass disk which receives light from the lamp of the instrument. The use of this luminous field has another advantage; to the patient it appears to surround the bright image of the target and thus reduces its apparent brightness.

§ 9. SPHERICAL ABERRATION AND IRREGULAR REFRACTION OF THE EYE

The method employed in the coincidence optometer gives the measure of the refraction of the small area of the system through which the light enters the eye relative to the axis of the emerging beam. In the case of an eye which is free from spherical aberration such a measurement would represent the refraction of that meridian, and by rotation of the apparatus about any axis which would allow both entering and emerging beams to remain within the pupil the refraction in the various meridians could be determined. But if the eye has zonal aberration a rotation of the apparatus about the axis of the pupil will allow us to measure the refraction of a single zone of the system; on the other hand, if the apparatus is rotated about some other axis in such a case, the result would show differences in the refraction of different meridians giving a false appearance of astigmatism. It will therefore be seen that some means must be provided by which the instrument can be accurately centred upon the pupil and which will also allow the operator to select the zone of the pupil to be tested.

In the instrument that has been developed by Messrs Taylor, Taylor and Hobson, these means have been provided. The optical details are given in Mr Reason's paper, and it is sufficient here to say that the rapid introduction of an auxiliary lens system into the viewing system permits the observation of the image of the patient's pupil which is formed within the instrument. In the plane of this image are situated the mirrors from which the light is reflected into the patient's eye, and a small area of light upon one or other of the mirrors is the effective source of light which is imaged again by the optometer lens in the plane of the patient's pupil. When the pupil-sighting system is in use the observer sees the image of the patient's pupil with the mirrors projecting into it. The image is divided and one-half is reversed by the viewing system. Mechanical adjustments in the base of the instrument allow the image of the pupil to be brought to the central position. A small patch of light upon the edge of one of the mirrors shows the position at which the light is entering the patient's pupil, and thus the zone of the pupil which is being tested. By means of a simply operated screw adjustment the position of this light relative to the axis of observation can be controlled, and thus various zones of the pupil may be selected.

In the usual routine test a measurement of the spherical aberration of the eye is not advocated, although in a case with a very large pupil the author has found a difference of refraction of 2 dioptres between the central and peripheral zones. In order to minimize the time required for the test it is usual to select an intermediate zone and to ensure that the instrument is centred upon the pupil at the moment of measuring the refraction in each meridian. It will be seen, however, that the spherical aberration of the eye may affect the spherical element of the result and prevent its agreement with the subjective measurement in some cases. The significance of this is discussed in the paper by Mr Briggs dealing with the clinical use of the instrument. The presence of spherical aberration will not affect the measurement of astigmatism, and it is this element of the refractive error which is the most difficult to determine by other methods. It is probable that the exact amount of the spherical correction must always be a matter for final adjustment.

Owing to the selective nature of the method, irregularities of the refraction of the eye become apparent. In some objective optometers provision is made for the measurement of the refraction in only one-half of the pupil; it is presumed that the eye must be either a spherical or sphero-cylindrical system and that the refraction in the two halves of the pupil will be equal. In the final development of the coincidence optometer provision is made for carrying out the test over the complete circle of the pupil so that irregular differences of refraction can be detected and measured. It is probable that no other method of measuring refraction provides a means for the detailed study of irregularities.

It is obvious that as lenses for the correction of vision must have either spherical or sphero-cylindrical powers irregular errors of refraction cannot be corrected, and for this reason they are the frequent cause of difficulties and loss of time in subjective testing. The rapid detection of irregular refraction which is possible with the coincidence optometer will avoid the loss of time occasioned by the apparently inconsistent answers given by the subject, but it is particularly important to be able to apply the results given by the instrument to obtain the best sphero-cylindrical correction of the irregular eye.

A further study of the subject is required, but as far as our clinical experience with the instrument goes it appears that the cases of irregular refraction can be placed in three groups. The commonest type is one in which the principal meridians of astigmatism are found to be symmetrical and the same in upper and lower halves of the pupil, i.e. when the instrument is set for meridian location and is rotated through 360° a meridian is found at every 90°. In spite of this symmetry the refraction, particularly the astigmatism, is found to be different in the upper and lower halves of the pupil, thus two possible corrections are found. In the majority of these cases either the weaker or the mean of the two corrections is preferred subjectively. Another type of irregular case is one in which only a small area of the pupil differs from the remainder, as would result from the presence of a small nebula of the cornea. In such a case the refraction of the small irregular area can be neglected in the prescription. The third type of case is the most difficult to measure and to prescribe for; it is one in which the refractions of various parts of the pupil have no relation to one another, the refraction being completely irregular. In such a case the visual acuity is subnormal and the irregularity becomes manifest when an attempt is made to locate the principal meridians with the optometer; many apparent meridians may occur at various angles bearing no apparent relation to one another. When this effect is found the best method of making the test is to measure the refraction at intervals of 10 or 20° round the complete circle of the pupil. From the results obtained a fairly satisfactory prescription can sometimes be deduced. If an area approaching half the pupil approximates to a sphere or sphero-cylindrical result this will usually prove to be the best correction, but if on the other hand there is no regular portion at all the best correction must be sought for subjectively.

In conclusion, it may be said that this instrument appears to provide a means of making some new investigations in connexion with the optical functions of the eye, in addition to its clinical use in the measurement of refraction. The provision of a duplicate fixation device for the other eye with a means for adjusting the convergence of the visual axis enables accurate objective measurements to be made of the amplitude of accommodation relative to convergence and also the study of changes in astigmatism with accommodation. Some preliminary tests with an experimental apparatus on these lines have given promising results, and it is hoped soon to make a full investigation of these problems.

§ 10. ACKNOWLEDGMENTS

Finally, I wish to acknowledge the helpful advice I have received from Mr H. H. Emsley, and the other members of the staff of the Applied Optics Department of the Northampton Polytechnic where the first model of this instrument was constructed. Also I wish to express my thanks to Mr R. E. Reason of Messrs Taylor, Taylor and Hobson, Ltd., for the admirable work he has done in the design and development of the final instrument, and to Messrs Clement Clarke, Ltd., who have supported the development and commercial production.

THE DEVELOPMENT OF THE FINCHAM COINCIDENCE OPTOMETER

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Received 30 *April* 1937. *Read* 3 *June* 1937

ABSTRACT. The optical and mechanical features of a commercial development of the Fincham Optometer are described. The instrument permits direct measurement of the cylinder axis and of the refraction in different zones of the pupil and through 360°; it incorporates means for transferring the focus from the retina to the pupil to facilitate alignment, and a fixation system for arresting the subject's accommodation.

§ 1. INTRODUCTION

The instrument about to be described is a commercial development of the Coincidence Optometer designed by Mr E. F. Fincham and described in the previous paper.

The aim has been to produce an instrument which incorporates the basic features of the Fincham Optometer and is suitable for manufacture, which is convenient to manipulate, and is robust and not dependent for its accuracy upon the perfection of its slides and bearings.

The considerations underlying the design of the instrument have been discussed in the previous paper, and the details of the present instrument will therefore be described without further introduction.

§ 2. OPTICAL CONSTRUCTION

The optical system, which is shown in figures 1 to 5, can be subdivided into four sections. The first is the target system, comprising the elements *G* to *L* and *OPQST*, whose function is to produce on the retina a rotatable image of the target, and to form within the instrument an image of the retina. The second section includes the elements *U* to *Z*, which form the reversing microscope through which this image of the retina is seen divided into two parts, one reversed with respect to the other. In the third section come the pupil lenses *M* and *N* (figure 5) which, when they are inserted into the system, transfer the focus from the retina to the pupil to facilitate alignment. The fourth section comprises the fixation elements *B* to *F*, whose function is to form on the retina, quite independently of the target used for measurement, an image of an auxiliary object for fixing the subject's accommodation and direction of sight.

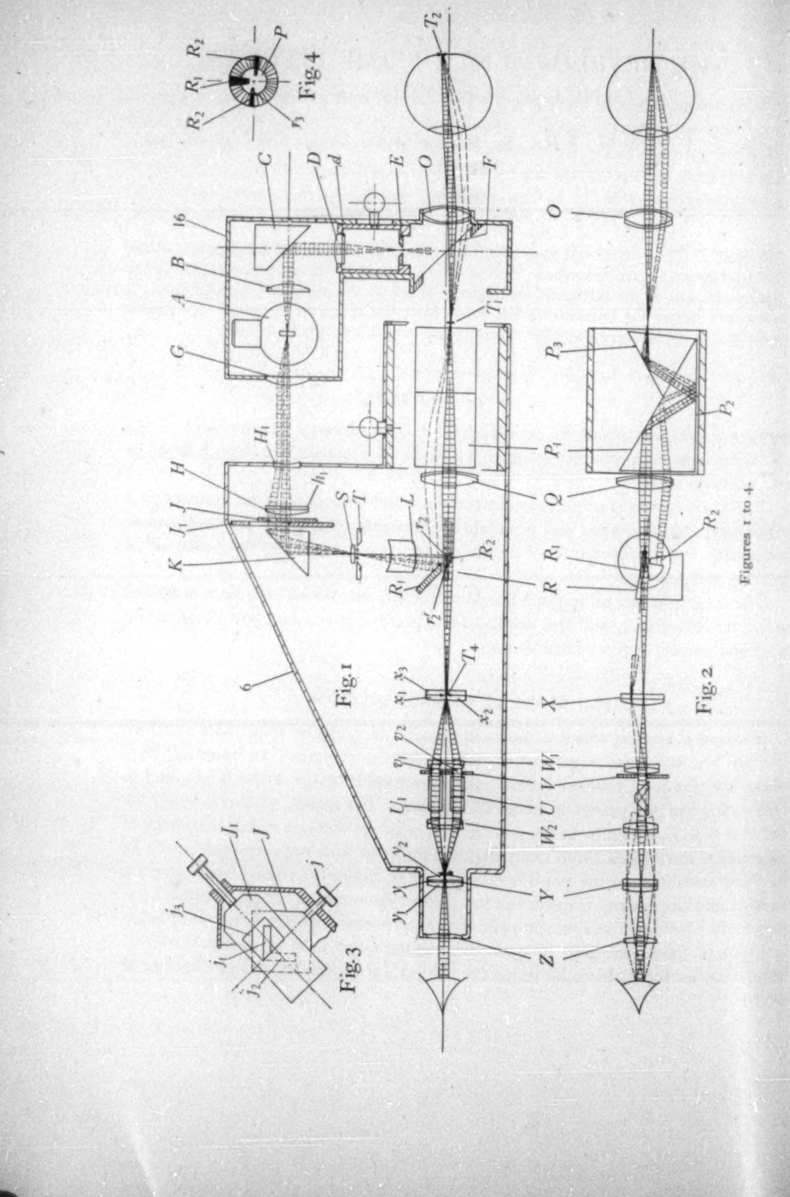
Fig.1
Fig.2
Fig.3
Fig.4
A
B
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d
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K
L
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Q
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U_1
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W_2
X
x_1
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y
y_1
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Z
6
16

Figures 1 to 4.

§3. THE TARGET SYSTEM

The target system is one in which the illuminating and observing beams pass through the same ophthalmoscope lens and is similar in principle to some that have been used before. The usual lens system, however, has been extensively modified to permit more varied measurements and to avoid some ghost reflections that were found very troublesome. The image to be observed is not very bright, and even the third-order ghosts have to be substantially eliminated.

Figure 1 and 2 show the system in side elevation and plan, the elements in the casing 16 being positioned at a fixed distance from the subject's eye, and the elements in the casing 6 being axially movable for measuring the refraction.

Light from the lamp A is collimated by the condenser G, and is then focused on the target T by the condensers H and H_1. These two lenses form an inverted telephoto lens, this construction being used merely to provide an image of the filament of suitable size in the required place. A real image of the target T reflected by the mirrors R_1 and R_2 is formed on the axis of the observing system at T_1 by the lenses L and Q, and an image of T_1 is then formed on the retina through the ophthalmoscope-lens O, which is mounted in the casing 16 with the pupil of the eye at its front principal focus. The target-image is focused on the retina by moving the casing 6 and hence the image T_1 along the axis. When the image is focused the lenses O and Q form an image of the retina suitable for observation at the virtual image of the target T_4 formed by the mirrors.

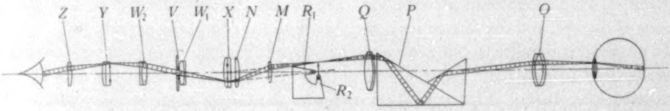


Figure 5.

The marginal area of the pupil through which the retina is illuminated is delimited radially by one or the other of two slits j_1 and j_2 in a mask J (figure 3) which is imaged on the mirrors R_1 and R_2 by the field lens S, and thence on the pupil by the lenses Q and O. The mirrors are mounted in the rear focal plane of the lens Q and are thus imaged on the pupil, together with the mask, independently of the separation of O and Q. A shutter, shown diagrammatically as a plate J_1, admits light to one slit or the other. The slits are tangential to and equidistant from the axis, and the mask J in which they are cut can be moved along their bisector by a screw j so that their distances from the axis, and hence the radius of the zone of the pupil being measured, can be varied. The areas at the pupil are delimited circumferentially by the width of the mirrors. The tips of the mirrors do not actually touch the axis, but leave a small central area through which the retina can be observed. This central area is actually defined by a stop in the reversing system, to be described later.

The images formed on the pupil and on the retina are rotated simultaneously by means of three rotatable reversing reflectors P_1, P_2 and P_3 which may be regarded as a Dove prism in which the refracting faces have been replaced by reflectors in order to avoid unsymmetrical aberrations. These reflectors have been made in the form of an internally reflecting prism with its faces normal to the axis; but it was found that a third order ghost, receiving two reflections off the same prism face, could only be eliminated when the face was exactly normal to the axis, and this led to such fine tolerances on the prism angles that the prism has now been replaced by a system of three first-surface reflectors.

It happens that the only ghosts off the lenses *P* and *Q* that are troublesome are the first order ghosts off the surfaces convex towards the incident light. For the reason that the aberrations of both lenses enter into the measurements, removal of the ghosts either by appreciable tilting or by extreme bending of the lenses is impracticable. The lenses work at $f/3$, and have to be allowed their most favourable form. Calculation and trial show that the ghost off the ophthalmoscope lens can be eliminated only when the target image is formed wholly to one side of the axis of the lens, but that the ghost off the second lens can be avoided only when the target crosses the axis. A further requirement is that wherever the target image is formed the images of the mirrors formed by the two lenses must be centred in the pupil of the eye. These conditions are satisfied by mounting the ophthalmoscope-lens on the axis of the eye, and the second lens, together with the rest of the system in the casing 6, on an axis parallel to but sufficiently displaced from the axis of the ophthalmoscope-lens to avoid the ghost which is then reflected away from the axis by the convex lens surface. This separation displaces the target image without displacing the pupil image, as the light imaging the pupil is collimated between the lenses. The prism rotates about the axis of the ophthalmoscope lens; the illuminating and observing beams are therefore rotated round the centre of this lens and no periodic errors due to traces of zonal aberration can arise despite the decentred lens system. When the eye is centred on the axis of the ophthalmoscope-lens, the beams also rotate round the centre of the pupil, and the retinal image of the target is rotated symmetrically round the axis of the eye. The target slit is radial to the axis of the eye and its centre is 3° off the axis. This arrangement permits the fixation object (to be described later) to be imaged centrally on the retina; it causes no error in the determination of the cylinder axis, and it has been found by experiment that even at twice this radius possible errors in the measurement of the refraction are of negligible magnitude.

The target is at a finite distance from the second lens which forms a half-size image of the target, and this arrangement has the advantage that the general direction of the light reaching the convex lens surface, by which the light is outwardly reflected, is already divergent from the axis; so that although the first order ghost inevitably enters the viewing system when the target beam sufficiently approaches the axis, a minimum radius of 1 mm. at the pupil can be attained.

§ 4. THE REVERSING MICROSCOPE

The elements in the reversing system have (1) to divide the field into two parts with a fine dividing line; (2) to hand the light passing through one half of the field; (3) to define the area of the subject's and the observer's pupils through which observation is made. The light passing through the two parts of the field must pass through the same area of each pupil.

The first element is a combined field lens and concave biprism *X*, mounted at the image of the retina with the roof of the biprism normal to the target line. The element comprises two convex lens segments x_1, x_2, whose centres of curvature are positioned one on each side of the lens-axis. They divide the light into two separated beams, and form two images of the pupil on a two-holed mask whose holes are correspondingly separated and define the single entrance and the single exit pupil of the observing system. The reversing prism *U* is mounted in one beam and a parallel-ended compensating block U_1 in the other beam. An objective W_1 collimates the light before it passes through the prism and block, and a second objective W_2 forms a further image of the retina and of the field-lens *X* on a second field-lens and convex biprism *Y* in the focal plane of the eyepiece. The second biprism is made in one piece to which the field-lens is cemented, and its functions are to superimpose the images of the two holes in the mask on the observer's pupil and to provide a clean dividing line for observation through the eyepiece.

The first biprism is mounted slightly nearer to the observer than the image of the retina; its dividing line, which has nominally to be superimposed on that of the second biprism, is therefore slightly out of focus and the useful result is that a narrow and sharply defined strip of the field at *X*, about 0·007″ wide, is suppressed. Small chips on the dividing line of *X* are therefore not seen and there is a reasonable tolerance on the alignment of the system.

This system, although it may seem elaborate, satisfactorily fulfils its functions, and since it is convenient to have a second image of the pupil at which to mount the mask *V* the system is not really wasteful of elements.

§ 5. THE PUPIL SYSTEM

The third group of elements comprises the two lenses *M* and *N* which are used for sighting on the pupil to ensure accurate alignment of the instrument with the eye. When these lenses are inserted into the system the images of the pupil and of the retina are transposed; and the images of the target form the pupils of the system, while the subject's pupil is focused in the eyepiece, as shown in figure 5. The image of the pupil is then seen through the eyepiece as a dull red disc illuminated by light diffused from the retinal image of the target (figure 4).

The insertion of the pupil-sighting lenses makes no difference to the image seen by the subject, and the same small retinal image of the target suffices for the whole process of adjustment and measurement.

In addition to the pupil image the arms of the mirrors R_1 and R_2 are seen projecting into it, because these mirrors are at an image of the pupil. Use is made of the presence of these mirrors to provide an indication of the radius of the pupil at which the illuminating beam enters it. For this purpose the upper edge of the horizontal mirror R_2, intercepting the shaft of light from the parallel slits T and j_2, is made roof-shaped; the polished face r_2 reflects light from the sharply focused image of the slit j_2 forwards towards the subject; the other face r'_2 is diffusive and scatters light from the same image backwards towards the observer. Through the eyepiece a slit of light r_3 is seen crossing the mirror R_2, as shown in figure 4, which indicates the area of the pupil P through which the light is entering it.

Further use is made of the pupil image to indicate when the instrument is at the right distance from the eye. This is of some importance in cases of considerable myopia or hypermetropia as the power-scale can only be calibrated for one distance. The method depends on the separation of the axes of the lenses O and Q, by virtue of which a movement of the instrument along the axis is accompanied by a movement of the image across the field in a direction which is vertical independently of the orientation of the rotating prism. The instrument is so made that if, after it has been aligned so that the pupil image remains stationary while the prism is rotated, the distance is adjusted until the pupil image is bisected by the dividing line of the field, the pupil will be correctly positioned at the focus of the ophthalmoscope-lens. In this way it is not difficult to set the distance within 1 mm. The correct distance also corresponds with the best definition of the pupil image, but owing to the exceedingly small numerical aperture of the system adjustment by focusing is generally not accurate enough.

The technique of adjusting the instrument in such a way that errors of distance and centering are not confused, although a little troublesome to describe, is easily mastered and is quite effective in practice.

§ 6. THE FIXATION SYSTEM

The last section of the optical system includes the elements B to F, which are used for fixing the accommodation and direction of sight. For this purpose a virtual image of an illuminated pin-hole E is formed on the axis of the ophthalmoscope-lens by a pellicle-mirror F which is so thin that it has no measurable effect on the transmitted target image. The pin-hole is provided with focusing adjustment independently of the target used for measurement. The brilliant ghosts inevitably formed off the ophthalmoscope lens and off the eye are eliminated by means of complementary colour filters. It happens that the retina is reddish in colour and reflects very little light of shorter wave-length than 5000 A. A yellow filter having a sharp cut at about this wave-length is therefore mounted in the viewing system at y, and a complementary blue filter in the fixation system at d. The ghosts are thus blue and are completely absorbed by the yellow filter, which, however, reduces the brightness of the observed image by a negligible amount. Since blue light is absorbed by the retina and cannot be used for measurement, a further yellow filter is mounted in the illuminating system at h, so that the blue wave-lengths are eliminated from the target image before the light reaches the eye, with consequent reduction in fatigue for the subject.

§7. GENERAL CONSIDERATIONS

The optical system has the useful property that the accuracy of measurement does not depend on precise alignment of the movable elements. The measured quantity is the separation of the two casings 6 and 16, and since the movement in the middle of the scale is 0·05 in. per dioptre there is no difficulty in providing a durable and accurate coupling.

Analysis shows that the stability of the system depends only on the relative positions of the target-slit, the mirrors R_1, R_2, the lens W_1, the reversing prism U, and to a much less extent on the lens L. For making measurements these elements are moved as a whole; they can therefore be securely mounted on a single frame and moved without fear of relative disturbance due to wear. But for this the mounting would have been both costly and liable to error, as a displacement of the slit of 0·0001″ is readily detected. All the other elements of the measuring system are common to both the illuminating and the observing beams, and lateral displacements of these elements therefore deflect both beams equally and introduce no errors. Thus accuracy in the slide and in the mounting of the rotating reversing reflector is not of fundamental importance, and ordinary manufacturing limits are more than good enough.

The change from axis to refraction measurements is effected not by displacement of an optical element but by displacement of an aperture relatively to fixed optical elements, and here again there is no need for great accuracy.

The design of the condensers permits both objects to be properly illuminated from the same lamp independently of their motion; and the inverted telephoto construction happens to be a considerably lesser evil than the mechanical difficulties that would have resulted from the use of a single condenser of suitable focal length.

The numerical aperture of the beams is generally exceedingly small, and in most positions a single plano-convex lens is perfectly satisfactory. The design has further been proportioned so that many of these plano-convex lenses have the same focal length and nearly all have the same diameter. For example, such diverse elements as the two lamp condensers, the slit field-lens, and the two pupil-sighting lenses, are alike. The manufacture of both glasses and cells is thereby greatly simplified.

§8. MECHANICAL CONSTRUCTION

The upper part of the instrument housing the optics is carried on a vertical shaft 1 (figure 6) supported in a sleeve 2 mounted on the base. The shaft can be moved vertically for height adjustment by a knob in the base and can be rotated for turning the instrument from one eye to the other by another knob also situated in the base. The shaft thus economically serves two purposes. The working distance of the instrument from the eye is adjusted by the knob 5, and the part of the system axially movable for measurement, which is housed in the box 6, is moved by the graduated wheel 7. The rotatable reversing prism is turned by the graduated wheel 8.

The internal construction of the optical section is shown by the drawings (figure 6), which show a plan and two elevations of the instrument, with a detail of the construction inset. The side elevation is sectioned in the axial plane of the lens system but the end elevation is sectioned in several planes for economy of space.

The upper end of the vertical shaft is forked to form two bearings 9 and 10 for a horizontal shaft 11, and to carry a bar 12. A bracket 13, clamped to the horizontal shaft 11, slidably engages the bar and keys the shaft against rotation. The shaft forms the main slide of the instrument and is movable longitudinally by the rack and pinion 14 and 15.

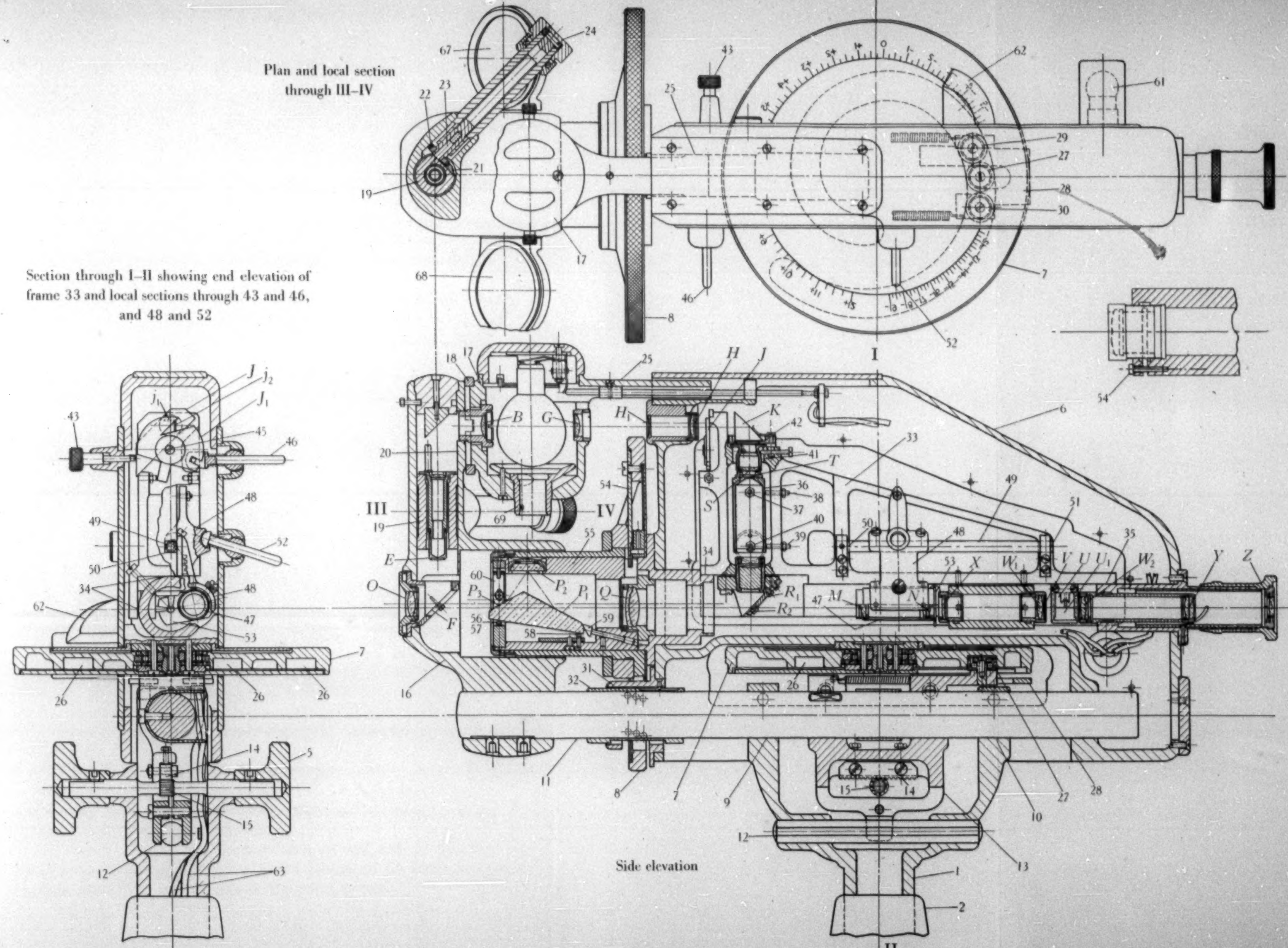
A casting 16, clamped to the extreme end of the shaft, carries the ophthalmoscope-lens *O* and pellicle-mirror *F*, the lamp house 17 which is heat-insulated from the casting by a bakelite spacing ring 18, and the fixation system 19. The fixation cell slides in a vertical hole 20, and is driven by the rack and pinion 21 and 22. A spring plunger 23 in the end of the pinion-shaft bears against a flat on the cell and, urging it anticlockwise, forces the involute rack teeth into the pinion to eliminate backlash. The mounting of the knob 24, which is graduated, permits adjustment of the zero.

The body 6 in which the axially movable elements are mounted, slides on the same horizontal shaft that forms the main slide and is keyed against rotation by an arm 25 projecting from the lamp house to engage a slot cut on the top of the body. The power wheel 7, by which the body is moved, is pivoted to the body on ball bearings; and a spiral cam slot 26 cut on the underside of the wheel engages a ball bearing roller 27, pivoted to the bracket 13. Backlash between cam and roller is taken out by two further rollers, 29 and 30, mounted on a spring loaded sliding plate 28. The directions of the resulting forces are so balanced that in spite of several pounds loading and a cam angle averaging 1 in 10 there is no appreciable force tending to drive the wheel, which turns equally freely in both directions. No provision is made for taking up shake in the pivot of the cam. The maximum shake permitted by the tolerances is equivalent to an error of 1/50th of a dioptre, and since no wear is to be expected in either of the hardened ball races the shake may be neglected.

To ensure easy motion of the body, the front slide bearing 31, which carries the greatest load, is a ball bearing slide. The balls are kinematically spaced by a cage 32.

The vital elements determining the zero adjustment are fixed to a frame 33. The frame has two surfaces at right angles forming a **V** machined along its under side in which the pupil mirrors R_1, R_2, the first biprism X, the collimating objective W_1 and mask V, the reversing prism U, and the compensating block U_1, are fixed. No ambiguity in the position of the reversing prism is permissible, and therefore in the plane of reflection the location of the prism is strictly kinematic.

The biprisms and the mask have to be accurately adjusted rotationally and then clamped in position; and the method of clamping is shown inset. The cell screws some distance into a tube, which is slit near the end rather more than half way across. The springy tongue thus formed is pulled down by the clamping screw 54.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Plan and local section through III–IV

Section through I–II showing end elevation of frame 33 and local sections through 43 and 46, and 48 and 52

Side elevation

Figure 6.

The thread in the tube is relieved in the plane of the slit to avoid burring the thread. Very little clamping pressure is required and the cells do not tend to rotate while the screw is being tightened.

The frame is kinematically suspended in the body by the engagement, at 34 and 35, of the ends of the **V** with the tubes supporting the lens *Q* and the eyepiece unit, and is keyed against rotation by means of a stud and clamping screw, not shown on the drawing, at the top of the body.

The target slit *T* is formed on the upper end of the tube 36, which is spring urged against four adjusting screws 37, 38, 39 and 40. The lower adjusting screw 40 is provided with a hexagon head and is accessible through a hole in the cover in case the need for zero adjustment should arise. It is worth mentioning that in spite of some rough handling, and the apparently crude constraints, the need for an external zero adjustment has not yet been felt.

The field lens *S* and the prism *K* are provided with adjustments for imaging the pupil apertures in the mask *J* correctly on the pupil mirrors, and the lamp filament correctly on the slit. The plate *J* slides along the bisector of the slits and is moved by a screw 43, with which it is held in contact by a spring. Light is admitted to the required slit through a gash in the shutter J_1 which is pivoted to the frame at 45 and moved by the lever 46.

The condensers *H* and H_1 are eccentrically mounted to permit lateral adjustment of the filament image in case the filament distorts after the lamp has been used for some time, although since new lamps are pre-focused this adjustment is not often required.

The pupil-sighting lenses are mounted one at each end of a tube 47, adjustably carried in a bracket 48. The bracket is mounted on a shaft 49, rotatable in **V**'s 50 and 51 formed in the frame, and is moved by the lever 52. When the lenses are in their inoperative positions the field of view is stopped down by a mask 53, carried on the end of the tube, to exclude some ghosts.

The rotatable reversing reflectors are carried in a cylindrical mount 55, which is rotated by means of the key 54 and the wheel 8. The reversing reflector P_2 is fixed in the side of the mount and the remaining two reflectors P_1, P_3 are formed in one piece and are adjustably supported on two screws 56, 57, at one end and on one screw 58 at the other end. The reflectors are pressed in contact with these and with the adjustable end-stop 59 by a **U**-shaped plunger 60, pressed down by a spring. The reflectors have to be adjusted so that the axes of the cylinder bearings on each side of the reflectors P_1, P_3 are virtual images of each other. The reflectors are made of glass and are aluminized.

The scales are illuminated by a scale lamp 61 on the side of the case, the power scale being seen and illuminated by reflection in a mirror 62. The lamp also illuminates the observer's note pad. Both lamps are wired internally, and the leads 63 up the pillar are aluminium-sheathed to prevent chafing.

The relaxation discs 67 and 68 are mounted one on each side of the lamp bracket and are illuminated through windows in the bottom of the lamp house. A shutter 69 obscures light from one window or the other, or both.

§ 9. MATERIALS

The materials from which the instrument is made are determined by their function and cost. The base and the sleeve mounted on it are of ordinary cast iron for cheapness. The vertical shaft 1 has a ground surface exposed just above the sleeve, and to minimize the possibility of rust the piece is cast in a nickel-silicon cast iron. The same material is used for the headrest on account of its malleability. Since the greater part of the optical system moves for taking measurements, the lightest possible materials have been used to avoid sluggishness due to inertia. The body is cast in a magnesium alloy, and the remaining castings are in aluminium with the exception of the sleeve containing the rotating reflector-mount, which is cast in gun metal. The power-wheel, in which is formed the cam-slot 26 engaging the rollers with line contact, must be light but hard, and is cast in a Rolls-Royce aluminium alloy having about one and a half times the Brinell hardness of *Y* alloy. The horizontal shaft is made of steel, case hardened and ground, and its exposed portion is chromium plated.

§ 10. ACKNOWLEDGMENTS

In conclusion, I would like to thank Mr Fincham, Mr Lee, and Mr Warmisham for their help and advice, and the Directors of Messrs Clement Clarke and Co. and of Messrs Taylor, Taylor and Hobson, Ltd., for their patience during the development, and for permission to publish this paper.

AN EXPERIMENTAL STUDY OF TURBULENCE DIFFUSION

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Received 28 *April* 1937. *Read* 25 *June* 1937

ABSTRACT. This paper describes a method involving study of the rate of diffusion, due to the turbulence prevailing in a stream, of a dye let into the stream. The concentration of the dye is measured with a beam of light and photoelectric cell, and the stream-velocity with a hot-wire anemometer, at various places in the stream. As a test of the method the latter is first applied to molecular diffusion and shown to give results in accordance with those obtained by other methods. Next, turbulence induced in a water channel by gratings of various mesh-widths is traced. By using a pair of sources and light-beams with associated photoelectric cells, the degree of correlation between the motions at two points in the turbulent stream, both along and across it, can be studied.

Finally the diffusion due to turbulence of the dye-source at the head of a plate edge-on to the stream is studied. Smooth plates and those having a sinusoidal roughness are used. It is found that both the velocity-distributions and the rates of diffusion can be expressed in terms of a Blasius parameter and a factor dependent on the wave-length of the roughness.

§ 1. INTRODUCTION. METHODS OF MEASUREMENT

The treatment of turbulence, and especially atmospheric turbulence, as a problem in diffusion is due in the main to G. I. Taylor(1), L. F. Richardson(2) and W. Schmidt(3). Whether the thing transported be called mass, energy or vorticity to suit a particular problem, the form of the resulting equations is the same. The first-named of these physicists has considered the turbulence produced in a channel by disturbing agencies such as honeycombs, and has shown that turbulence as a type of diffusion is intimately related to two other concepts which have proved fruitful in hydrodynamics in recent years, viz. the idea of a correlation coefficient between the conditions at two points in a stream, and that of the mixing-length or mean free path of a disturbance nascent in a stream before it mingles with the circumambient fluid.

The theoretical work of L. F. Richardson was supported by observations of the width of smoke trails from tall chimneys, and Sutton(4) has carried out more extensive measurements of diffusion in the atmosphere. The general principle of diffusion-measurements necessitates the introduction into the fluid of some material or energy whose subsequent distribution can be determined by the analysis of instrumental records. If energy be introduced it may take the form of (A) an inexorable oscillation of fixed frequency and amplitude, or (B) a constant supply of heat. If mass-transport is to be studied the source may take the form of (C) colour or (D) a solid such as smoke, dust or silt.

Method (A) has been used by the writer and E. Tyler(5). Part of the boundary of a small wind channel run at subcritical speed was oscillated in simple harmonic motion, and the spread of the disturbance was traced downstream with a hot-wire detector. The difficulty in such experiments is that the disturbance in the boundary layer tends to change the character of the flow in the main stream, so that something more than a mere diffusion of the oscillation may result.

Experiments of class (B), in which heat was introduced along a line-source transverse to the channel, have been described by Schubauer(6), and some others made by Simmons are cited by Taylor(7). The temperature across various downstream sections may be measured with a thermocouple and hence the rate of diffusion of heat can be calculated, although Schubauer determined three points only on each traverse, viz. that of maximum temperature and those where the temperature was half the maximum. The diffusion so observed is, of course, the combined effect of turbulence-transport and heat-conduction, as in most cases of forced convection. In the same category belong the experiments of Townend(8) who traces the diffusion of isolated masses of heated air ("hot spots") by the methods of *schlieren* photography.

It may be opportune at this point to compare the advantages and limitations of the four methods. The hot-wire apparatus (A) for tracing fluctuations of velocity possesses the advantage of compactness. It gives the nearest approach to a point-to-point delineation of conditions in the stream, whereas the optical methods involve a beam covering a certain area, of which the minimum workable size is probably 10 mm^2. On the other hand, the indications of the hot-wire detector are a function not merely of the amplitude of the velocity-fluctuations but also in a marked degree of the *average velocity* about which those fluctuations take place, so that near a solid boundary a considerable correction is necessary for the change in mean velocity from point to point—a correction which may amount to several hundred per cent of the reading.*

With regard to (B) and (D), the colour method possesses the advantage of producing no appreciable local change of density or viscosity in the fluid. The specific gravity of the solution corresponding to the maximum coloration recorded in the turbulence measurements described later in this paper is 1·005.

In the heat-diffusion method, the source must be at a high temperature and this causes a distortion of the flow by gravity, unless the channel has a vertical axis. Further, the coefficient of thermal diffusivity for air (0·2 c.g.s. unit at 50° C.) is a greater fraction of the turbulent diffusion than is that of molecular diffusion of a dye such as potassium permanganate ($1{\cdot}3 \times 10^{-5}$ c.g.s. unit); hence a larger correction, amounting to 10–15 per cent in Schubauer's experiments, is necessary in the observed temperature-distribution due to this molecular conduction.

§ 2. TECHNIQUE OF PRESENT METHOD (C)

In the present method a dye such as potassium permanganate is let into a water channel along a horizontal line perpendicular to the direction of flow. The dye dissolves and is diffused downstream by the intermingling with neighbouring strata of the fluid passing the source, and the time average of the colour-density at any level (x, y) is measured by a horizontal beam of light traversing the channel and falling upon a photoelectric cell. At first the dye was introduced by siphoning a concentrated solution through a narrow tube, mounted transversely to the stream and pierced at the after edge with a number of small holes. It was found that the tube tended to induce turbulence in its wake. Further, any velocity relative to the main stream which the jets might have on emergence was also a disturbing factor. Latterly a thin phosphor-bronze strip, 2 mm. by 0·3 mm., was stretched tightly across the stream and this, painted with a soluble gum and the finely powdered solid dye, acted as the line source. Several seconds elapsed before the gum was dissolved off and the dye began to colour the stream, so that the fitting of the source in position was not accompanied by a vivid overall coloration of the stream such as resulted when the powder was directly applied to the strip.

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* Cf. reference (5), figure 2.

The channel was constructed with plate-glass sides and extending between two reservoirs with a capacity of 10 cubic feet. The upstream reservoir was fed by a pipe from the city main at a head of 90 ft., while on reaching the downstream reservoir the water ran over a weir of adjustable height to the waste pipe. Level-gauges could be adjusted to touch the water-surface at intervals along the channel. The channel was 6 ft. long and 10 in. wide, and the maximum depth of water was 1 ft.

It was of course necessary to establish a relation between the colour-density of the diffusing dye and the photoelectric current in the cell, which was illuminated by a horizontal beam of light interrupted by the colour. The voltage at which the photoelectric cell gave a linear response to intensity of illumination was first found by trial, and then a small portion of the channel was sealed off to form a tank into which solutions of known concentration of the dye were introduced in turn, and the response of the cell to light passing through the solution was measured. It was found that over the range of colour-density likely to be used in the experiments a linear relation existed between the concentration and the current-defect, i.e. the difference between the reading of the galvanometer with clear water and that with the dye in solution.* The clear-water reading was maintained constant during the experiments by adjusting the width of the beam whenever necessary. The latter was normally 1·5 cm. wide and 2·5 cm. deep. The velocity was measured with a calibrated hot wire of nickel, 0·002 in. in diameter, which was held on a fork. Both hot wire and photoelectric cell with its associated beam of light could be traversed in the x, y plane through the water.

§ 3. THEORY OF THE METHOD: MOLECULAR DIFFUSION

When the laws of probability are applied to diffusion in fluid motion,† the probability considered is that of finding a given concentration c at any position

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* This relation does not correspond exactly with the well-known law of Beer, but it must be remembered that that law applies to monochromatic light. In the present experiments, the author was concerned only to get the most sensitive and convenient response of the apparatus to changes of colour-density, and the relation quoted was found to give the best fit.

† H. Gebelein has recently written a general account on this problem(9).

(x, y, z) in the field over a given small interval of time δt. This probability-distribution will be a function whose dimensions are the reciprocal of a time. The first moment of this will be another function which may be called the *expectation*; it has the dimensions of a velocity U, and is in fact that of the fluid conveying the dye. We then have

$$\frac{\partial c}{\partial t} + c.\nabla U + U.\nabla c = k.\Delta c \qquad \text{......(1)},$$

where k is a diffusion constant having the dimensions $[L^2 T^{-1}]$. If u_1 is the observed mean velocity with which the dye spreads, we must have also if there is no loss of dye

$$\frac{\partial c}{\partial t} + c.\nabla u_1 + u_1.\nabla c = 0 \qquad \text{......(2)}.$$

If $U=0$, we shall then have the case of molecular diffusion at a rate u_0, when (1) becomes

$$\frac{\partial c}{\partial t} = k.\Delta c \qquad \text{......(3)};$$

otherwise we may expect that $u = U + u_0$, so that (2) becomes

$$\frac{\partial c}{\partial t} + c.\nabla\,(U + u_0) + (U + u_0).\nabla c = 0 \qquad \text{......(4)}.$$

In most practical cases of fluid motion, the velocity u_0 of pure diffusion is negligible in comparison with that of the fluid U.

In order to test the new method against an experiment for which the results by other methods were available, the molecular diffusion of potassium permanganate in water was followed in a narrow cell measuring 3·5 × 0·7 × 20 cm. through which the beam of light passed parallel to the narrow edge. This cell was mounted in the large channel, filled with slowly running water to act in some measure as a thermostat. The cell was nearly filled with water, and some saturated solution containing excess powder was carefully run to a depth of about 1 cm.; finally a film of oil was added on the top to prevent evaporation. Measurements of the vertical gradient of concentration as indicated by the photoelectric cell were made from day to day for a week, figure 1 *a*. There was sufficient saturated solution at the bottom of the cell for this to be considered a level of maintained saturation, although it is true that the exact level at which the concentration began to fall as a result of diffusion may have become lower during the week. The appropriate solution of equations (1) and (2) for diffusion along the y-axis alone is

$$\frac{\partial c}{\partial y} = \frac{c_0}{2\sqrt{(\pi k t)}} \exp\,(-y^2/4kt) \qquad \text{......(5)}.$$

Thus the slope of a $\{y^2, \log_e(\partial c/\partial y)\}$ line is equal to $4kt$. Such curves for various values of t in days are shown on figure 1 *b*, and the mean slopes are plotted against time in figure 1 *c*. One notes the departure from straightness which these lines exhibit at large concentrations, a result to which three causes may contribute: (1) the coefficient of diffusion is known to be relatively greater at large concentrations, (2) the point of departure ($y=0$) from maximum concentration is known to shift somewhat, and (3) the method is uncertain at high concentrations of the dye.

The last point requires elaboration. When the dye is highly concentrated the cell is working close to its dark condition, so that the current is small and difficult to measure. There is, however, another difficulty. The last equation shows that the gradient of concentration is large where the concentration itself is large, and this causes a marked diffraction of the light-beam depending on the width of the cell that lies in the path of the beam. (This diffraction is, in fact, the basis of diffusion measurements in Wiener's method.) Examination of the light passed by the cell as a whole on to a screen shows that the dispersion is small with such a narrow cell, but it is a disturbing factor to be reckoned with in wide tanks and large gradients of concentration. Fortunately turbulence diffuses a dye so rapidly that such gradients are scarcely to be encountered in work other than that dealing with molecular

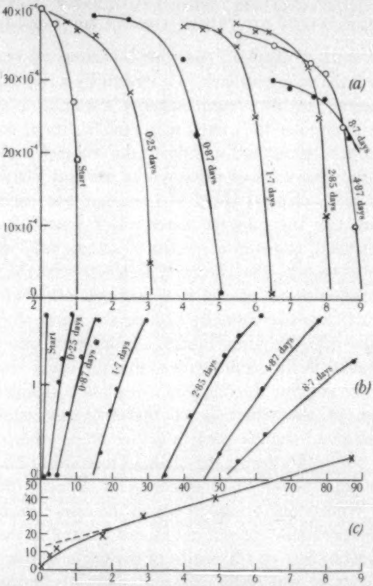


Figure 1. Molecular diffusion.

	Ordinates	Abscissae
(*a*)	*Concentration* (*g.*/*cm.*³)	*y* (*cm.*)
(*b*)	$log_{10}\,(\partial c/\partial y)$	y^2 (*cm.*²)
(*c*)	$log_{10}\,\{y^2/(\partial c/\partial y)\}$	*Time* (*days*).

diffusion. The refractive index of the solution at the concentrations used in the subsequent experiments varied between 1 and 1·005, so that dispersion was a negligible factor. If the straight part of the curve of figure 1 *c* is extrapolated to an arbitrary time origin, the mean coefficient of diffusion works out at $1{\cdot}3 \times 10^{-5}$ cm.^{2}/sec., agreeing well with values given by other methods.

§ 4. DIFFUSION OF TURBULENCE BY A GRATING

The theoretical work of Taylor(7) and the experimental work of Schubauer(6) indicate that the turbulence engendered in a stream by a regular series of slots is a function of the spacing. In the present instance a number of gratings were constructed of horizontal circular rods fixed in a vertical frame with equal spacing.* A grating was introduced about half way down the channel, and the space between it and the end of the channel was traversed in vertical planes with the optical detector. At first a mean channel speed of 4 cm./sec. was used, the water supply being from the mains and the coloured water run to waste. Later, a 2-h.p. circulating pump was installed, allowing of speeds of 20 cm./sec., which correspond to a Reynolds number of 60,000. The difficulty now was that the water returning to the channel was contaminated by the dye and coloured before it reached the grating. This difficulty was overcome by making the water slightly acid and bubbling sulphur dioxide into the pump intake. An attempt was made as follows to reduce the permanganate at the correct rate so that the water returned colourless to the channel. When the sulphur dioxide was in excess it decolorized the fresh dye coming from the source; the reduction was therefore made somewhat incomplete so that the water remained slightly pink in colour on re-emergence. An auxiliary fixed beam of light was sent athwart the channel to another photoelectric cell upstream of the model, and the out-of-balance current between the two photoelectric cells was read on a Wheatstone bridge in which the cells formed one pair of ratio arms. With this compensating device it did not matter if the reduction of the permanganate was incomplete on the return of the water to the channel. It should be added that the channel was given sufficient slope to produce uniform flow as estimated by traversing a hot-wire anemometer across the experimental section.

In turbulent motion, diffusion from the source occurs at rates governed by the velocity-fluctuations, to which we may assign the components u', v', w'. Of these u', parallel to the axis of the channel, is disguised by the much greater general velocity of the stream U, while w' across the channel cannot register impressions in the beam of light which runs in the same direction and therefore averages out any variations of concentration in this dimension. There remains only the vertical component of the turbulent diffusion, so that the equation reduces to

$$\frac{\partial c}{\partial t}=k\,\frac{\partial^2 c}{\partial y^2} \qquad \text{......(6).}$$

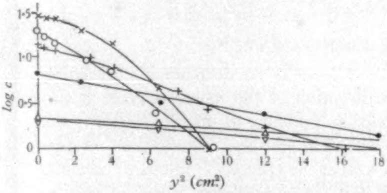
The solution is formally similar to equation (5), but instead of $2kt$, which had the

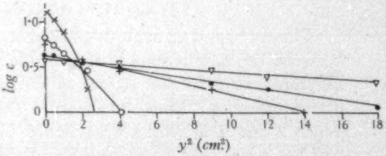
* Schubauer actually used honeycombs. Gratings were preferred by the writer for greater ease in construction, and not because it was thought that two-dimensional flow would be induced thereby.

dimensions of the square of a length, we may, following Taylor⁽⁷⁾, write $\overline{Y^2}$, where $\overline{Y}$ is the mean vertical distance diffused in the time t that corresponds to a general drift of the whole field through a distance x, so that $t=x/\overline{U}$, $\overline{U}$ being the mean velocity of drift. The gradient of concentration on the left of equation (5) is replaced by the concentration itself, since the dye is only supplied at $x=0$, and not all along the axis of the channel. When $\overline{U}$ is constant, the distribution of the dye in any vertical plane will be given by

$$c=\frac{c_0}{2\sqrt{(2\pi)}\,\overline{Y}}\exp\left(-y^2/2\overline{Y^2}\right) \qquad \ldots\ldots(7),$$

c_0 being the (maintained) concentration at $(x, 0)$. $\overline{Y^2}$ will be given by the negative slope of the graph of y^2 against log c. Such graphs are given on figures 2 and 3 for two different speeds, with the source 10 cm. downstream from the grid. A slight curvature at regions near the source was attributed to local variations in $\overline{U}$. Figures 4 and 5 show how $\overline{Y^2}$ varies with x, that is with time, as the stream flows away from the source. The initial slopes of these curves are, for a given value of $\overline{U}$, measures of the turbulence induced by the grid. It is this slope that is proportional to the mesh-size of the grid. This statement holds for the present results provided the grids are geometrically similar, but there is also an effect due to the bars of the grid





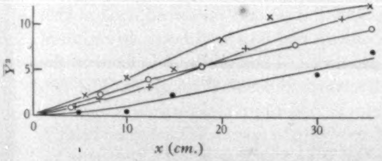
Diffusion due to turbulence induced by a grating.

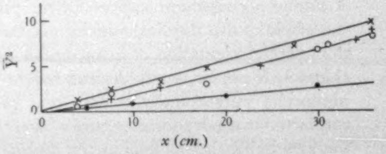
Figure 2. $U=1·5$ cm./sec.

	×	○	+	●	▽	△
x	4	8	12	23	33	43
Mean Y^2	1·25	1·8	3·3	7·7	11	13

Figure 3. $U=2·5$ cm./sec.

	×	○	+	●	▽
x	4	8	13	23	43
Mean Y^2	0·5	1	2·8	7·5	11·5





Decay of turbulence downstream from grating.

Figure 4. $U=1·5$ cm./sec.

Figure 5. $U=2·5$ cm./sec.

	×	+	○	●
Mesh of grating (in.)	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{16}$	$\frac{3}{16}$
Bar of grating (in.)	$\frac{3}{8}$	$\frac{3}{16}$	$\frac{3}{8}$	$\frac{3}{16}$

as well as the mesh. Thus the grid with $\frac{3}{8}$-in. bars and spaces does not induce the same turbulence as that with $\frac{3}{16}$-in. bars and $\frac{3}{8}$-in. spaces. Further, if the turbulence is isotropic, as seems to be the case in most channels, we may write for the slopes of these curves

$$\sqrt{\overline{Y^2}}/x = \sqrt{\overline{v}'^2}/\overline{U} = \sqrt{\overline{u}'^2}/\overline{U},$$

where $\overline{u}'$ and $\overline{v}'$ are the amplitudes of velocity-fluctuation in the component directions. Dissipation of turbulence after the stream leaves the grid will result in a reduction of $\overline{u}'$ and $\overline{v}'$, with decrease of slope of the $\overline{Y^2}:x$ curves, as it were a reduction of diffusion constant with concentration of vorticity. This decay is slow in the writer's channel, possibly owing to accretion of turbulence from the floor, but the commencement of decay may be observed as a diminution in slope on the extreme right of figures 4 and 5.

§ 5. CORRELATION OF FLUCTUATIONS

Closely bound up with this diffusion of turbulence is the decrease in correlation between the fluctuations in magnitude and direction of the mean velocity at two different points in the stream at corresponding epochs, to which Taylor(7) has drawn attention. Thus, to measure the correlation between fluctuations at two points *A* and *B* on a line perpendicular to the axis of the channel at identical instants, two hot wires may be mounted and the magnitude and relative phase of the respective potential-differences induced in them by the turbulence compared. Prandtl and Reichardt(10) do this by bringing each potential-difference to one pair of plates in the cathode-ray oscillograph. The figure traced by the electron spot then depends on the correlation coefficient between the fluctuations in potential-difference, being a circle when the coefficient of correlation is 1, and a straight line when it is 0.*

In adapting the optical method to the measurement of correlations one proceeds as follows. A thin glass tube lets in dye from an orifice pointing downstream at the point *A*, and at the same point a pencil of light restricted by diaphragms to a diameter of $\frac{1}{2}$ cm. crosses the channel horizontally to one of a pair of matched photoelectric cells. A similar arrangement suffices for the point *B* with a second photocell, except that the whole of this duplicate device can be racked up and down without alteration of the relative orientation of lamp, orifice and photocell. Thus while *A* is fixed in the channel, *B* can be at any desired height in the vertical plane through *A*. The two photocells were connected with two variable 10,000-ohm resistances, a rectifier connected to a galvanometer, and a battery of 200 volts to form a Wheatstone bridge, the idea being that as long as the *déroulement* at *A* and at *B* remained the same no current would pass through the rectifier, but as the correlation between *A* and *B* became less, an increasing but, of course, alternating current would pass through the rectifier, and in consequence the mean deflection of the galvanometer would increase. To indicate the relation between this deflection and the correlation, and in some measure to act as a calibration of the apparatus, the sources of the water and the dye were removed from the channel and a disc driven by a motor was mounted in the channel. The circumference of the disc was cut in the shape of an epicycloid with two cusps. When the two cells were mounted at opposite ends of a diameter and the disc was rotated, the light on each cell varied in simple harmonic fashion but in the same phase, so that no deflection was recorded on the galvanometer. One cell being kept fixed, the other with its associated beam was moved round the circumference of the disc, the deflection increasing as the light fluctuations got out of step, until at a phase-difference of π (corresponding to an angular separation of the cells of $\pi/2$) the deflection reached a maximum, to fall again as the cells approached the diametrically opposed positions. In this way, a calibration curve, figure 6, of deflection plotted against phase-difference was obtained.

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* Actually it is the correlation in *resultant* fluctuations which is measured, though theory discriminates between u' and v' in this respect. Neither the optical nor the double-hot-wire method discriminates between directions of fluctuation, but in isotropic turbulence this does not matter.

The correlation coefficient as usually defined between a fluctuation u_1' at station A and that u_2' at station B is

$$R=\frac{u_1'.u_2'}{\sqrt{(\bar{u}_1'^2.\bar{u}_2'^2)}}.$$

When u_1' and u_2' are simple harmonic motions of equal frequency and amplitude, but having a phase-difference of δ, this expression reduces to $\cos\delta$. Approximate proportionality between galvanometer deflection and the cosine of the phase-difference is indicated by figure 6. Accordingly it was assumed that when the procedure was applied to the stream in the channel the deflection of the rectifier-galvanometer would measure the correlation coefficient directly, with the help of this calibration curve.

The pair of cells and associated light-beams were then arranged in a vertical plane across the channel, and the dye was let in from two jets just upstream of the light-beams. While one was kept still, the other was moved to various heights and the galvanometer deflection was noted when the cells were connected in the circuit described above.

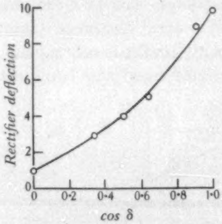

Figure 6. Calibration curve for correlations.

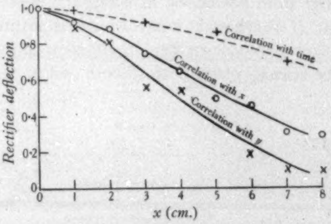

Figure 7. Correlation in turbulence due to a grating.

The two correlations, across the stream and down the stream, with one beam at a fixed point 20 cm. behind the $\frac{3}{8}$-in. grating are shown by continuous lines in figure 7. As Taylor indicates from theoretical considerations, the correlation with x is much closer than that with y, although the type of correlation here measured is not quite the same as that considered by Taylor, since the present measurements are concerned with the relative phase as well as the magnitude of the fluctuations.

Another type of correlation can be measured by comparing the oscillation at station A with that at B downstream, after allowing sufficient time to elapse for the general current to pass from A to B. A length of photographic film must then intervene between the records of the respective fluctuations. The two beams of light after passing perpendicularly across the stream were inclined by small-angled prisms until focused side by side on the film in continuous movement through a camera at known speed,* figure 8. The dye caused fluctuations in the intensity of the light, revealed as variations in blackness of the film on development. The film was then passed again through the two light-beams and cells, one for each half of the film, with the cells connected in circuit, but the pick-up for B was proportionately lower down the film than for A—somewhat after the fashion in which light and sound are picked up from a talking film—so that the galvanometer deflection measured the correlation between A and B after the proper time interval had elapsed. This correlation with time is shown by a dotted line in figure 7. In the absence of dissipation, a disturbance would be conveyed with unchanged amplitude down the stream, but in fact the correlation gradually departs from unity as the time increases. This type of correlation is analogous to that obtained by Townend[(8)] from the observation of the passage of hot spots downstream.

§ 6. TURBULENCE DIFFUSING FROM A BOUNDARY

The complete theory for the diffusion of turbulence from a solid boundary has yet to come and there are few experiments on the subject other than those on the heat-losses from hot plates, in which the matter is complicated by a temperature-gradient. It was thought that it would be of interest to apply the present apparatus to the securing of related data on diffusion and velocity-gradients near a plate edge-on to the stream, plates both smooth and of determined roughness being used.

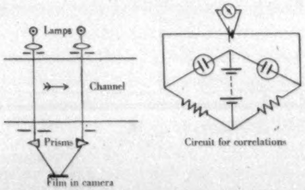

Figure 8. Correlation apparatus and circuit.

Smooth plates of varnished wood and brass having a width equal to the full width of the channel and either 30 or 60 cm. long were used. The wooden plates were bevelled at the leading edge, and for the slower speeds the linear dye source was let in as a fillet to the front edge. The brass plate used at the higher speeds has a circular tube of the same outer diameter as the thickness (2 mm.) of the plate soldered along the front edge and pierced with a few small holes. The dye was fed to this source through vertical tubes coming down the sides of the channel. The only new experimental difficulty was that in the passage of the beam of light just above the surface of the plate some light was reflected into the photoelectric cell, so that the clear-water reading of the cell differed in this region from the more distant ones and made a measurement of the darkening produced by the dye less certain than at places remote from the plate. This influence extended to about 3 mm. from the surface of the plate. The hot-wire measurements of velocity in this region were corrected for proximity to the plate by the method devised by Piercy and the writer(11).

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* A single wide beam was used when x was less than 2 cm.

For the rough plates it was decided to idealize the roughness into a sinusoidal boundary having an amplitude equal to half the wave-length λ. These were constructed of a series of equally spaced wires set transversely to the stream and soldered on a plate. Wax was then run on to the plate, and when it had hardened it was gouged out of the interspaces to the set template. The three constructed had $\lambda = 0{\cdot}5$, $\lambda = 1$, and $\lambda = 1{\cdot}6$ cm. respectively, and troughs of depth $\frac{1}{2}\lambda$. The plates were mounted in mid-stream, in a region of (originally) uniform velocity. The velocities in the neighbourhood of the smooth and the two roughest plates are shown on figures 9, 10 and 11. To conform with the Blasius theory of skin friction(12), the velocities are plotted against the parameter ξ, equal to $\sqrt{(Uy^2/kx)}$ where k now represents the dynamical coefficient of viscosity. In fact, the broken line drawn in figure 9 represents the Blasius distribution, for comparison with the experimental points. In figures 10 and 11, y is measured from the tops of the undulations, which admittedly afford an uncertain zero, but at this level the distribution of velocity does show a steeper gradient than the smooth plate, which does in some measure serve as a criterion of the roughness. The gradients for the three rough plates were

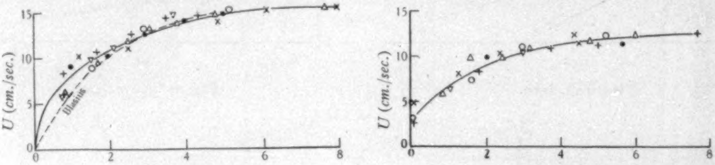

Figure 9. $\lambda=0$.

Figure 10. $\lambda=1$ cm.

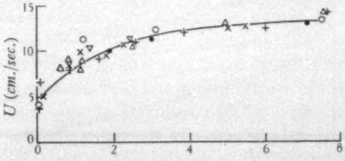

Figure 11. $\lambda=1{\cdot}6$ cm.

Figures 9, 10, 11. Velocity-distribution along plates. The symbols refer to values of x corresponding to those in the following diffusion figures.

in the ratio 4 : 5 : 6, as nearly as could be estimated. The observed distributions satisfy, except very close to the boundary, that postulated by Prandtl (13), i.e.

$$U + a \log (\xi + b)$$

where a and b are constants dependent on the roughness so that the gradient

$$\frac{\partial U}{\partial \xi} = \frac{a}{\xi + b}.$$

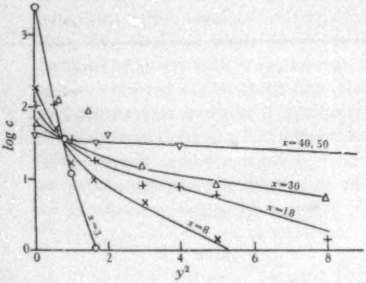

Figure 12. $\lambda=0$.

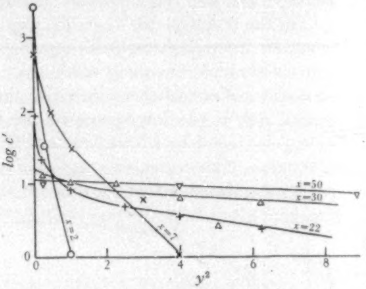

Figure 13. $\lambda=1$ cm.

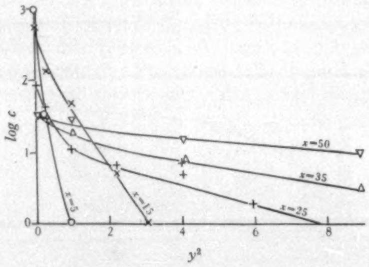

Figure 14. $\lambda=1{\cdot}6$ cm.

Figures 12, 13, 14. Diffusion of turbulence along plates.

Measurements of the concentration of the dye in various planes perpendicular to the plate, at distances x from the leading edge, were made, but before $\{\log c, y^2\}$ curves could be plotted a correction had to be made for the gradient of U near the surface of the plate. In consequence of this velocity-gradient the diffusion appears more rapid at first as the dye leaves the plate. In actual fact the concentrations recorded for small values of y represent a proportionately higher value of t than those for larger values of y and the same value of x. It will appear that the velocity v of scattering in the direction perpendicular to the plate is nearly constant, whereas the drift velocity parallel to the plate increases outwards, and the average velocity $\overline{U}$ where

$$\overline{U} = \frac{1}{\xi}\int_0^{\xi} U\, d\xi$$

had to be determined for each value of x, y. Hence the time taken for particles of dye to reach a given co-ordinate (x, y) was calculated by using the curves of figures 8, 9, 10 and integrating the necessary areas under the curves. The equation corresponding to equation (7) is then

$$(\log c_0 - \log c)\,.\,\overline{U} = \xi^2/Y^2 \qquad \text{......(8)},$$

U (contained in ξ) being the drift velocity of the whole stream in the absence of the plate. With the introduction of this correction factor the $\{\log c, y^2\}$ lines become nearly straight, figures 12, 13, 14, although there is still a tendency for the velocity of diffusion to increase over the first few millimetres from the plate as well as with time. The former increase may be accounted for by an hypothesis that the vortices originate from a level slightly above the level of the plate or of the crests on it. The latter increase is brought out by the $\{\overline{Y^2}, x\}$ curves, figure 15, which indicate that vorticity is added to the stream by its passage over the plate, and particularly over the rough plates for which a rapid increase of slope of the $\{\overline{Y^2}, x\}$ line occurs as the stern is approached. This rate is roughly proportional to λ. The short smooth plate shows a less rapid growth, with the usual dissipation occurring beyond the stern (with decreasing slope). The importance of the parameter ξ can be shown in respect of these diffusion measurements, as well as in relation to velocity-gradients, for it is possible to reduce all the measurements for a given plate to a single curve by plotting them against $1/\xi^2$. In figure 16 this has been done for the smooth plate. The slopes of the lines in figure 12, *uncorrected* for variation in drift velocity, are plotted against y^2/x.

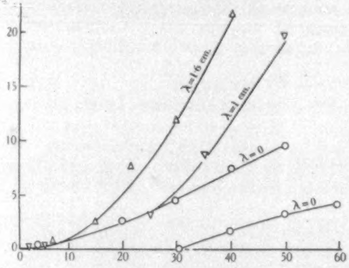

Figure 15. Growth and decay of turbulence along plates.

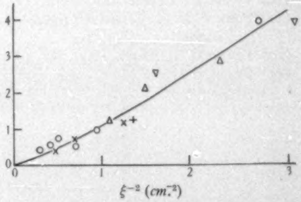

Figure 16. Growth of turbulence along smooth plate in relation to Blasius parameter.

§7. ACKNOWLEDGMENTS

The author wishes to express his indebtedness to Prof. W. E. Curtis and the Research Grants Committee of Armstrong College for the facilities to carry out this work, and to Prof. G. I. Taylor for much helpful criticism and advice during the course of its execution.

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THE VORTEX MOTION CAUSING EDGE TONES

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Received 10 *April* 1937. *Read* 25 *June* 1937

ABSTRACT. A detailed investigation has been made of the tones produced when a jet of air strikes an edge, with velocities extending from the lowest possible to those in the neighbourhood of the Reynolds critical velocity in the orifice. Four different stages of stable vortex-formation occurred and the whole phenomenon was found to lie within the sound-sensitive range of the jet. Throughout this range the dependence of the frequency n on the distance h of the edge and the mean velocity U can be closely represented for a 1-mm. slit-width and a wedge of angle 20° by the formula

$$n = 0{\cdot}466\, j\, (U-40)\, (1/h - 0{\cdot}07),$$

where $j = 1$, 2·3, 3·8 and 5·4 for the four stages respectively.

The stage represented by $j = 1$ may occur simultaneously with the other stages and thus two notes of different pitch may be produced. Comparison with the vortex motion in sensitive jets shows marked similarity, but it cannot be assumed that the vortex motion in edge tones has its origin at the orifice, as it always has in sensitive jets.

§ 1. INTRODUCTION

It was first noted by Sondhaus⁽¹⁾ in 1854 that tones can be produced by blowing a jet of air against an edge, and that a resonating column, such as is always found in musical wind instruments is not essential. In the eighty years following, the subject has received the attention of many investigators and it has been realized that vortex motion plays a large part in the production of sound. It was reasonable to expect, therefore, that the information gained by the detailed examination of the vortex motion in jets subjected to sound and the author's theory of the mechanism of sensitivity⁽²⁾ would be of use in attempting a more comprehensive explanation of the phenomena of edge tones than has hitherto been possible.

It has, however, unfortunately been found necessary to repeat much of the work of former investigators. The reasons for this were: (1) arguments have been made from analogies with water jets which have led to conflicting conclusions⁽³·⁴⁾; (2) in most cases only the pressure has been measured from which the velocity of the jet cannot be obtained with certainty; (3) some writers maintain that as many as six jumps in tone may occur⁽⁵⁾ while others have denied that any occur at all if sufficient care is taken in the experimental arrangements⁽⁶⁾; (4) the jumps in frequency have been commonly stated to be in simple numerical relation (e.g. in octaves), and this in the absence of resonators is *a priori* unlikely; (5) the experimental methods adopted in obtaining some of the material leave the interpretation of the results open to considerable doubt(4, 6, 8); (6) no systematic and thorough examination has been made which would enable a formula for the frequency to be deduced. The formulae given involve assumptions with regard to Kármán vortex-sheets which are quite inadmissible and yield results which are only approximately correct(3, 9).

§ 2. EXPERIMENTAL METHOD

The apparatus used was that described in detail in former papers(2, 10).

A brass wedge of angle 20° and width 5 cm., and having a height of 7·5 cm., was suspended from a mounting by which it could be raised and lowered and also moved across the orifice by a delicate screw motion. It could also be set accurately parallel to the orifice in the vertical plane. The mounting was attached to an iron bar which was screwed on to the outside of the wooden box containing the slit. This formed a very rigid system and was carefully adjusted so that when the wedge was raised its edge remained always in a plane passing through the centre of the slit and parallel to its sides. The under side of the movable slit was slightly modified so as to be accurately symmetrical and this made the stream of air flow in such a manner that it was accurately bisected by the wedge at all heights.*

The stroboscopic disc was, when necessary, covered with insulation tape so that only three slits were uncovered and this allowed of photography at frequencies as low as 20 c./sec., although the intensity of the illumination was thereby reduced fourfold. In addition a separate stroboscopic disc was used for observation and the visual determination of frequencies. It was found convenient to have two rows of viewing-holes in the disc, one with 12 holes and a subsidiary one with 24. Any danger of running the disc too slowly at a fraction of the correct speed when the former row is being used can be obviated by observing through the latter, when the well-known doubled appearance should be seen.

All the films and nearly all the observations refer as in the former paper to a jet width of 1 mm., depth 1 cm. and length 2·3 cm.

§ 3. VARIATION OF FREQUENCY WITH EDGE-DISTANCE WHEN THE VELOCITY IS CONSTANT

The variation of the frequency n of the sound with the distance h of the slit from the edge when the mean velocity U of the stream is constant has never been thoroughly investigated, although for limited regions it has been observed that the product nh is approximately constant(11, 9, 12, 8).

The procedure adopted in this present research was as follows. The velocity was adjusted to a given value and the apparatus was left for half an hour to attain a steady state, the pump working against a leak in the manner formerly described.† Then the time for 50 to 100 litres to pass the gas-meter was observed and these readings were taken throughout the whole period during which measurements of h

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* Cf. reference (2), p. 714.

† Reference (2), p. 704.

and *n* were being made. Thus a series of times were recorded from which the mean velocity could be obtained and which showed that the velocity had been constant. All frequencies under 300 c./sec. were observed visually through the stroboscopic disc to which a counter working over a period of 15 sec. was attached. The mean of several observations was taken. The visual method was essential since no clearly audible sound occurs below 500 c./sec. Above 500 c./sec. the frequency was found by the method of beats with the calibrated heterodyne oscillator. It was found to be of the greatest value in obtaining beats to be able to decrease the output of the loud-speaker until the intensities of the two beating sounds were approximately equal. The height *h* was measured with calipers. The results obtained by visual means are shown in figure 1 and those obtained aurally in figure 2. In both cases the frequency is plotted against the reciprocal of the height of the wedge. The width *d* of the slit was 1 mm.

In every case it is clear that each curve consists of four distinct portions each of which is very nearly a straight line. The curve for $U=984$ cm./sec., shown in figure 2, is typical and can be considered in detail.

Starting with the wedge close to the orifice ($1/h=\infty$) no tone is heard, as is well known, until a certain minimum height is reached. This is represented by the point *N*. A clear bright tone then commences and the frequency decreases with increase in *h* until a point such as *L* is reached. The tone then jumps suddenly to *J*, but in certain cases, viz. those in which the velocity is above about 600 cm./sec., it is possible for the original tone to persist as well, and this gives the dotted portion *LZ*. At *Z* the lower note becomes inaudible. The upper note decreases in frequency with increase in *h* but at a more rapid rate than in the first case. On arrival at *H* a second jump takes place to *F* and the note again falls to *D*, and then a third jump to *B* occurs, when a weak tone drops to a confused irregular noise at *A*. From the point *F* onwards the original tone is again heard as well and gives the portion *YX*. There are therefore four clearly defined stages which will be referred to as stage I (*NL*), stage II (*KH*), stage III (*GD*) and stage IV (*CA*).

If now the curve is retraced in the opposite direction, i.e. if the wedge is lowered downwards towards the orifice, the sequence of events is not exactly the reverse of those occurring when the wedge is raised. Starting again at *A* the frequency rises now to *C* and then drops suddenly to *E* in stage III, from which point the frequency rises to *G* before falling suddenly to *I* in stage II. It increases then to *K*, from whence it drops to *M* and rises to *N*, at which point it ceases abruptly. In this case stage I is audible throughout the whole range, and persists in addition to the higher notes, where these occur. This is brought about by the fact that in certain circumstances stages I and III may be possible while I and II are not, a condition which occurs in the region *FGIH*. If stage II is in progress between *I* and *H*, stage I is not possible. But if stage III is in progress, stage I is possible as well and the region *YZ* occurs with *FG*. Thus the stage I is complete from *X* to *N* when we pass from left to right across figure 2, i.e. with the wedge approaching the orifice.

This fact accounts for a very confusing observation which can be made at the value of *h* corresponding to the points *Z*, *I* and *G*. At this height a jump in tone is

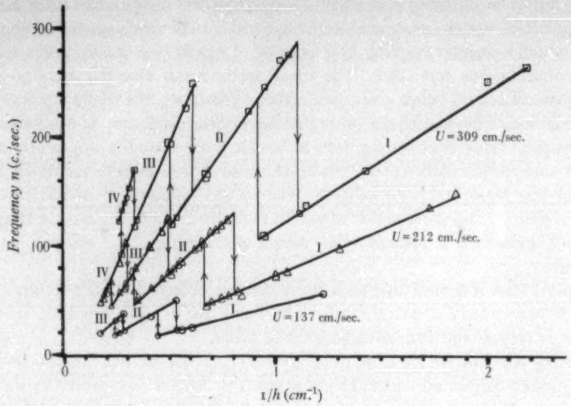

Figure 1. Variation of frequency with reciprocal of wedge-distance for low velocities.

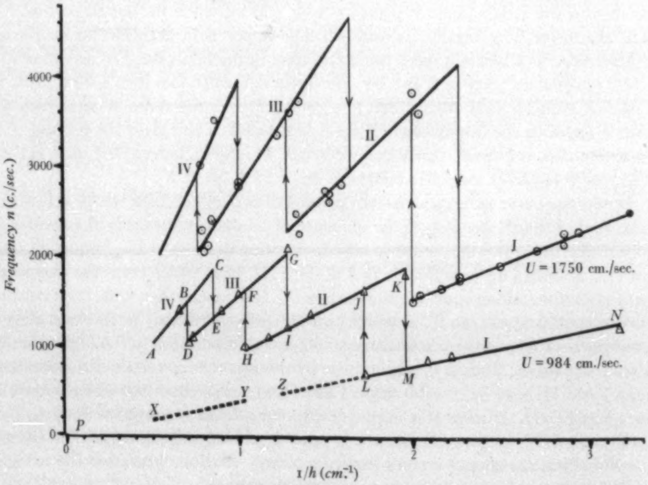

Figure 2. Variation of frequency with reciprocal of wedge-distance for high velocities.

heard which can be recorded as a jump up or a jump down according to whether the investigator is concentrating attention on the lower or upper note, i.e. he may hear the sequence of tones represented by *XYZIJK* or *EFGIJK*. This confusion is made possible by the fact that the intensity of stage I changes suddenly at *Z*. When stage I occurs with III it is easily audible but when combined with II in the neighbourhood of *Z* it is nearly inaudible. The intensity of stage I does not change appreciabiy in the region corresponding to the jump *DBCE*, and the possibility of confusion does not arise so readily.

The phenomenon mentioned above is probably the explanation of some otherwise curious results obtained by Richardson* which give a graph of n against $1/h$ consisting of a line sloping upwards and then a jump *upwards* to another line of increasing frequency. It seems possible that Richardson has recorded only the lower note and has therefore plotted the curve *XYZIJK*.

Again, the occurrence of stage I simultaneously with the other stages when the velocity is high, which was noted long ago by Wachsmuth(7), is probably the cause of Benton's assertion that if sufficient care is taken no jumps in tone occur at all(6).

A detailed study of his description indicates that the jumps took place in his experiments but that changes in intensity of the various components led him to infer that only the quality of stage I gradually altered.

In the graph under discussion ($U=984$ cm./sec.) the intensity of the sounds produced in stages II and III appears to the ear to be about the same, and much greater than in stage I. For high velocities (2000 cm./sec.) the intensities in stages I, II and III are nearly equal. Stage IV is very weak and unstable, and in the case of the lowest velocity, 137 cm./sec., it could not be observed at all.

It was discovered by inspection that all the points lie very nearly on straight lines radiating from a point P on the $1/h$ axis at a distance of 0·07 from the origin, and in figures 1 and 2 the straight lines are drawn so as to pass through this point.

§ 4. THE FOUR VORTEX STAGES

The four possible vortex stages are illustrated in figure 3, plate 1. For this purpose the stroboscope was set rotating so as to produce 126 interruptions of the illumination per second. The velocity was kept constant at a convenient value, 272 cm./sec., and the wedge was slowly raised until first of all a stationary view of stage I appeared. Photographs were taken and then the wedge was raised again until a second stationary appearance, showing stage II, was obtained. In a similar manner stages III and IV also were photographed, the frequency and velocity in each being constant. The distances of the wedge were $h=0{\cdot}81$, $1{\cdot}73$, $2{\cdot}65$ and $3{\cdot}5$ cm. The photographs show the four different ways in which one and the same frequency can be produced with a given fixed mean velocity of the stream.

In the former paper on sensitive jets(2) it was found that

$$\omega=\pi n,$$

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* Reference (8), figures 6 and 10.

where ω is the angular velocity of the leading filament of the vortex in radians per second, and this result was also found in the present research.

Since ω depends only on n, and n is constant in figure 3, the angular velocity is the same in each case and equal to 63 rev./sec. If the filament, on its first appearance, is taken to subtend an angle θ equal to 0 at the centre of the vortex then the values of θ at the edge are approximately as follows: In stage I $\theta=0$, in stage II θ lies between $\pi/2$ and π, in stage III θ lies between $3\pi/2$ and 2π, and in stage IV $\theta=5\pi/2$. Examination of the vortices formed in sensitive jets by sound showed that the vortex ceases to entrain air, revolution of the filament slows down and ceases, and the boundary of the jet is closed, at a certain distance from the orifice.* This is a distance corresponding to θ between 2π and 3π and so it seems that once the boundary of the stream is closed and the rotation ceases, the disturbance which maintains the periodicity in stages I to IV no longer occurs, since stage V is unstable.

The vortex-formation after the edge has been passed depends on the stage. In stage I the vortices complete a revolution and start a fresh series caused by friction with the wedge-face rotating in the opposite direction, and a vortex-street is thus formed. This is shown by the first photograph in figure 3 in the plate†, and in its most striking form in figure 4. In stages II to IV the vortices continue upwards, apparently little affected by the presence of the wedge. No sign of a secondary series forming a vortex street occurs.

The heights of the wedge which produce the same frequency with a constant velocity are examined in detail in table I. It will be seen that if the heights are called h_1, h_2, h_3 and h_4 for the stages I to IV, then the distances between them (h_4-h_3), etc., are, for the higher velocities, nearly but not quite constant. This agrees with some results for $U=562$ cm./sec. and $d=1{\cdot}02$ mm. found by Rieth⁽¹²⁾, but Schmidtke⁽³⁾ inferred from them that the distances were constant and hence that a Kármán vortex street must be present, an inference which is not supported by the present research.

Table 1

n (c./sec.)	h_4 (cm.)	h_3 (cm.)	h_2 (cm.)	h_1 (cm.)	h_2-h_1 (cm.)	h_3-h_2 (cm.)	h_4-h_3 (cm.)	U (cm./sec.)
20	—	5·68	3·92	2·02	1·90	1·76	—	137
100	3·48	2·41	1·57	0·75	0·82	0·84	1·07	212
150	3·33	2·50	1·64	0·79	0·85	0·86	0·83	309
1200	1·74	1·28	0·79	0·34	0·45	0·49	0·46	984
2400	1·58	1·15	0·75	0·33	0·42	0·40	0·43	1750

§5. THE VARIATION OF FREQUENCY WITH VELOCITY

A careful investigation of the variation of n with U when h is constant was made with values of h from 3·5 cm. downwards, with jets of width 4, 3, 2, 1, 0·5 and 0·25 mm. There is a close resemblance between the forms of the graphs of n against U obtained for all jet-widths, and it was found that as the jet-width decreased, the

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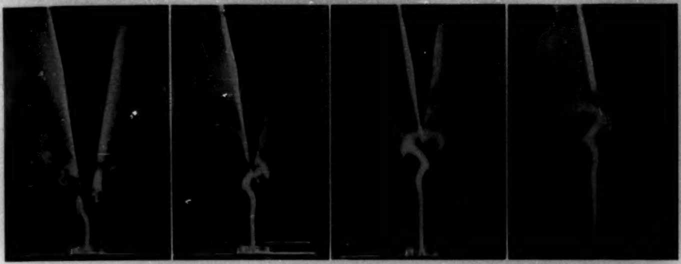
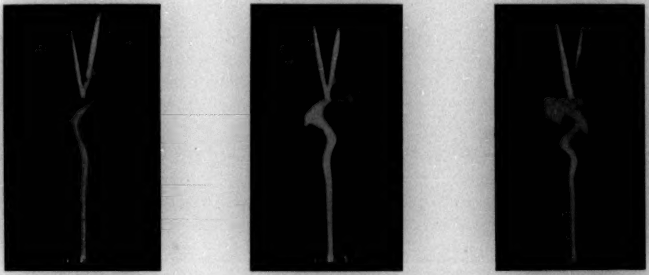
* Reference (2), p. 708. † The photographs on the plate have been reduced in the ratio 6 : 5.



Stage I $h=0\cdot81$ cm. Stage II $h=1\cdot73$ cm. Stage III $h=2\cdot65$ cm. Stage IV $h=3\cdot5$ cm.
$n=126$ c./sec. $U=\text{const.}=272$ cm./sec.

Figure 3. The four stages in vortex formation producing the same frequency.



Stage II $n=25$ $U=162$ cm./sec. Stage III $n=75$ $U=254$ cm./sec. Stage IV $n=126$ $U=272$ cm./sec.

Figure 6. Three vortex formations produced with a constant wedge-distance $h=3\cdot5$ cm.

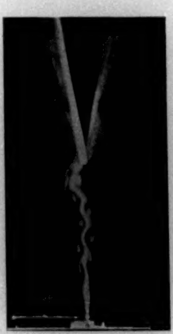


Figure 9. Sound $n=102$ c./sec. superimposed on edge tone $n=20\cdot5$ c./sec. $h=3\cdot5$ cm. $U=127$ cm./sec.

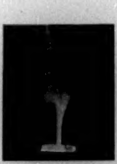


Figure 7.

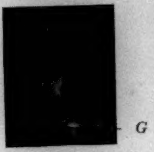


Figure 8.

Simultaneous production of two sounds of different pitch.

Fig. 7 $\begin{cases} n_1=210 \text{ c./sec. stage I} \\ n_3=800 \text{ c./sec. stage III} \end{cases}$

Figure 8. $n_1=210$ c./sec. suppressed by beard G.

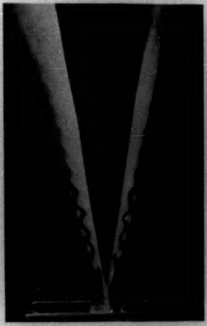


Figure 4. Vortex streets in stage I
$n=126$ c./sec. $h=0\cdot6$ cm.
$U=210$ cm./sec.

The photographs on this plate have been reduced in the ratio 6 : 5.

frequency of a given stage became lower for the same velocity and height. This is in agreement with some results obtained by Carrière⁽⁴⁾. The present discussion will be confined to a jet of 1 mm. In this case, when $h=3\cdot5$ stage I is not obtained; the first sign of oscillation is found when $U=120$ cm./sec. and $n=17$ c./sec. (stage II). As the velocity is increased the amplitude of the vortex motion becomes greater, and when U equals about 230 cm./sec. and $n=38$ c./sec. stage II suddenly ceases and stage III appears, the frequency jumping to 66 c./sec. With further increase in the velocity, the amplitude of stage III grows, and when $U=310$ cm./sec. and $n=99$ c./sec. the frequency jumps to 146 c./sec. (stage IV), and this continues till $U=330$ cm./sec. and $n=160$ c./sec. After this point no periodic motion is observed and the jet resembles a turbulent jet without a wedge. If now the velocity is reduced slowly, stage IV lasts until $U=200$ cm./sec. and $n=95$ c./sec., and then the motion jumps to stage III which lasts until $U=150$ cm./sec. and $n=38$ c./sec. The motion then jumps to stage II and continues down to the initial point where $U=120$ cm./sec. and $n=17$ c./sec. In each case the amplitude decreases. The three curves are slightly convex to the axis of U, approaching a straight line as the higher values of U and n are reached.

An attempt was made with U and h constant, to get different amplitudes and therefore possibly different frequencies, but this was not successful and it was concluded that U and h determine the vortex motion and therefore the frequency completely. It may be noted that U must be greater than about 500 cm./sec. for sound to occur. As h is decreased the range of the vortex motion increases: figure 5 shows n plotted against U, for h having the values 1·5, 1·0, 0·75, and 0·5 cm. The stages are indicated and it will be seen that each stage is linear, and when produced backwards towards the origin, cuts the axis of U in the neighbourhood of the point $U=40$ cm./sec.* On the same graph are also plotted the limits above and below which the jet exhibits no sound-sensitivity. These are taken from the former research,† together with extra observations made specially. The graph indicates clearly that, by means of the jumps, the edge tones remain within the central region of the sound-sensitive area.

An illustration of stages II to IV in the case where $h=3\cdot5$ cm. is given in figure 6, plate 1.

§ 6. MEASUREMENT OF THE WAVE-LENGTH

As in the former research on sensitive jets⁽²⁾, a series of films were taken in order to determine the wave-length λ, i.e. the distance between two successive vortices on the same side of the stream. A different convention with regard to the definition of λ was, however, found necessary. As was stated in the paper referred to, the estimation of the distance between the centres of two successive vortices is easy when the vortex-development is not great (and this applies to most of the results in that paper) but becomes increasingly difficult with greater development. In the case of edge tones the vortex development is always very marked, and therefore, in view of the fact that the central portion of the stream, which does not form into rotating filaments, presents a wave-like appearance, λ was defined to be the distance between successive troughs. When comparison with the films of sensitive jets was made, therefore, these films were re-measured with the new convention. This results in an increase of about 28 per cent in λ.*

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* To avoid confusion only a few of the observed values are plotted on the graph.

† Reference (2), figure 7.

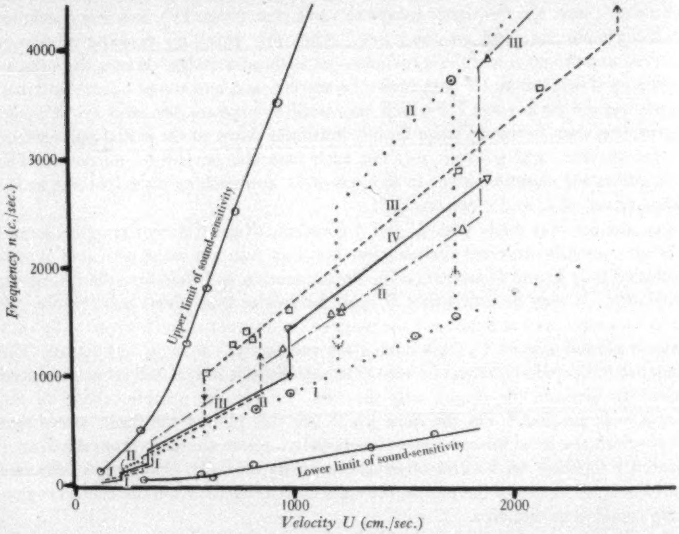

Figure 5. Range of edge-tone production: —▽— $h=1{\cdot}5$ cm.; ---□--- $h=1{\cdot}0$ cm.; —·△·— $h=0{\cdot}75$ cm.; ···⊙·· $h=0{\cdot}50$ cm.

Table 2 shows the results obtained for various values of h, U and n. The final column gives the value of $2hn/JU$, which according to König should be approximately unity. The comparisons with the results found for sensitive jets (where the vortex motion was produced by a loudspeaker in the absence of any wedge) show that there is no appreciable difference in the vortex motion in the two cases, and the steadiness of the relative vortex velocity u/U at all heights of the wedge confirms this conclusion.

Only one result for stage I is included, since the definition of λ is not clear in this case: it is assumed here that $\lambda = h$.

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* In table 2 of reference (2) this convention would only alter some 1-mm. jet values viz. 8B, 8C, 17C and the right hand column.

It should be noted that if cases are chosen in which the velocity is approximately the same, then the wave-length for a given stage increases with the distance of the wedge; compare, for example, stage II 28 B with 27 F, and 28 C with 27 G.

Table 2.

Height h of wedge (cm.)	Reference number of film	n (c./sec.)	λ (cm.)	U (cm./sec.)	u/U	Stage J	h/λ	$\frac{2hn}{JU}$ $J=1$, 2, 3 or 4
3·5	25 A, B and C	97	0·85	215	0·38	IV	4·1	0·79
3·0	*8 C comparison*	*97*	*0·90*	*237*	*0·37*			
	26 A and B	97	0·93	248	0·36	III	3·2	0·78
	C	194	0·68	321	0·41	IV	4·4	0·91
	8 D comparison	*194*	*0·51*	*253*	*0·39*			
2·5	*8 B comparison*	*97*	*0·75*	*185*	*0·39*			
	26 D	97	0·81	210	0·37	III	3·1	0·77
	E	194	0·77	380	0·39	III	3·2	0·85
	F	291	0·56	391	0·42	IV	4·5	0·93
	G	388	0·57	508	0·43	IV	4·4	0·95
2·0	27 A and D	97	0·89	227	0·38	II	2·2	0·85
	B	291	0·57	422	0·39	III	3·5	0·91
	C	388	0·59	550	0·42	III	3·4	0·94
1·5	27 E	97	0·78	200	0·38	II	1·9	0·73
	F	194	0·64	345	0·36	II	2·3	0·84
	G	291	0·64	502	0·37	II	2·3	0·87
1·0	28 A	97	1·00+	268	0·36+	I	1·0	0·72
	B	291	0·45	342	0·38	II	2·2	0·85
	C	485	0·43	517	0·40	II	2·3	0·94
1·17	40 A	800	0·36	616	0·47	III	3·2	1·01

It is also clear that h/λ is not a whole number, as it has often been assumed to be(5, 9, 26). Table 3 records the results obtained when the height of the wedge was kept constant at $h = 3{\cdot}5$ cm. and the velocity was varied almost throughout its whole possible range. A striking feature is the constancy of the wave-length throughout each stage. In stage III, for instance, the velocity can be doubled without alteration of λ.

§ 7. FORMULA FOR EDGE TONES

The fact that in figures 1 and 2 all the lines when produced backwards cut the $1/h$ axis near $1/h = 0{\cdot}07$, and in figure 5 the U axis in $U = 40$, allows a simple formula for the frequency in terms of the velocity of the stream and height of the wedge to be derived. The gradient $n \div 1/h$ for each stage was found to be closely linear with U. The formula obtained for a 1-mm. slit, a wedge of angle 20°, and air at 20° C. was

$$n = 0{\cdot}466\, j\,(U - 40)\,(1/h - 0{\cdot}07),$$

where j has the values 1, 2·3, 3·8, 5·4 for stages I, II, III and IV respectively. This formula gives the frequency correctly within 6 per cent for frequencies from 20 to

5000 c./sec. and with velocities from 120 to 2000 cm./sec. Graphs plotted for jets from 4 mm. to 0·25 mm. indicated that a similar formula would hold in these cases also, but the determination of the constants, a research in itself, was not attempted. The limits of h were found to be 0·31 cm. and 6 cm. The lower limit, however, rises when the velocity exceeds the Reynolds critical velocity for the given slit-width, reaching, for instance, 0·34 cm. at 3000 cm./sec.

Table 3.

Height of wedge = 3·5 cm.

Reference number of film	n (c./sec.)	λ (cm.)	U (cm./sec.)	u/U	Stage J	h/λ
36 A, B, C, G and H	20	1·51	138	0·22	II	2·3
32 A and B	21	1·56	142	0·23	II	2·2
33 B	25	1·51	162	0·23	II	2·3
34 A	29·5	1·50	187	0·24	II	2·3
35 C_1	36	1·55	200	0·28	II	2·3
35 F	36	1·00	140	0·26	III	3·5
33 C	50	1·05	185	0·28	III	3·3
35 C	53	1·02	186	0·29	III	3·4
35 A	58·8	1·04	210	0·29	III	3·4
34 C and D	59	1·07	212	0·30	III	3·3
35 D	71·5	1·08	245	0·31	III	3·2
33 E	75	1·02	254	0·30	III	3·4
32 C	84	1·11	277	0·34	III	3·2
33 A	84	1·00	271	0·31	III	3·5
31 F	89	1·02	283	0·32	III	3·4
31 F	125	0·90	283	0·40	IV	4·0
37 A	126	0·87	272	0·40	IV	4·0
35 G	143	0·88	305	0·41	IV	4·0
34 B	147	0·81	311	0·38	IV	4·3

§ 8. SIMULTANEOUS PRODUCTION OF TWO DIFFERENT FREQUENCIES

Visual observation did not disclose any vortex motion of more than one frequency until a velocity of about 600 cm./sec. was reached, and this, it should be noted, is just above the velocity when sound first becomes audible; see § 3. When this velocity is attained, the vortex system in stage III begins to oscillate from side to side as a whole, resembling the motion of stage I. It is, in fact, stage I superimposed on a stream already disturbed by stage III, and this can clearly be seen in figures 7 and 8, which illustrate the case in which $h = 1{\cdot}17$ cm., $U = 616$ cm./sec., and $n = 210$ c./sec. in stage I and 800 c./sec. in stage III. In figure 7 both motions occur together. Stage I is shown with a vortex just forming on the left side of the edge; cf. figure 3. The marked widening of the jet before it reaches the edge, however, shows that it is already turbulent, and if a glass plate G is introduced as shown in figure 8, stage I is prevented and stage III then shows up clearly in a similar phase to the illustration above it in figure 6. The vortices are not well defined because the photograph was taken with the stroboscope running at 200 c./sec. while the frequency was 800 c./sec.; consequently about half a period instead of an eighth of a period was illuminated at each instant, with the result that the outlines are blurred. The stroboscope could not be run at higher speeds, and high speed is not desirable in any case since sound which affects the jet is then produced.

The simultaneous production of two different frequencies commences with part of stage III accompanied by stage I. As the velocity increases, stage I accompanies other stages. This is indicated by the experiments recorded in table 4, for which U is constant and h is slowly increased.

Table 4.

U (cm./sec.)	Stages accompanied by stage I	Range through which stage I accompanies	n observed (c./sec.)	n calculated (c./sec.)	Remarks
583 to 725	III				
1200	II	Half way, till $h=0{\cdot}74$			
	III	Half way, till $h=1{\cdot}20$	600, when $h=0{\cdot}81$	645, when $h=0{\cdot}81$	
	IV				Stage I difficult to distinguish
1520	II	Half way			
	III	All			
	IV	All			Stage I, not clear
2000	II	All			Intensity of stage I varies throughout the range
	III	All	$n_1=1180$, $n_3=5040$, when $h=0{\cdot}70$	$n_1=1240$, $n_3=4730$, when $h=0{\cdot}70$	
	IV	All			
2030	II	All	$n_1=1400$, $n_2=3480$, when $h=0{\cdot}59$	$n_1=1510$, $n_2=3480$, when $h=0{\cdot}59$	
	III	All			
	IV	All			

These results indicate that the frequencies in stage I, when accompanied by other stages, are about 7 per cent lower than anticipated. It must be remembered, however, that the formula may in some cases have an error of 6 per cent: it may be concluded therefore that stage I remains practically unaltered when accompanied by other vortex motion.

In the case illustrated in figure 7 it could easily be proved, by listening through a rubber tube, that the sound from stage I came from a small region extending from the edge upwards, whereas the sound from stage III came from a millimetre or two below the edge where the vortices were entraining air.

§ 9. THE DISCONTINUITIES OF FREQUENCY

In view of the many assertions that have been made that the frequency-changes are octaves or some other simple intervals, it is necessary to examine the results of the present research in detail.

Table 5.

Velocity (cm./sec.)		Stage				Ratio			
		I	II	III	IV	I	II	III	IV
137	Up	17–39	18–29	—	—	2·29	1·61	—	—
	Down	56–	49–22	37–23	—	—	2·23	1·61	—
212	Up	45–105	47–75	45–66	47–	2·33	1·60	1·46	—
	Down	144–	130–57	126–76	104–70	—	2·28	1·66	1·49
309	Up	107–236	120–195	92–130	120–	2·21	1·62	1·41	—
	Down	263–	285–130	246–150	172–120	—	2·19	1·64	1·43
984	Up	700–1660	980–1650	1060–1510	—	2·37	1·68	1·42	—
	Down	1300–	1900–800	2080–1240	1860–1320	—	2·37	1·68	1·41
1750	Up	1560–3680	2300–3650	2060–2940	2000–	2·36	1·59	1·43	—
	Down	2550–	4160–1770	4640–2960	4000–2800	—	2·35	1·57	1·43

Mean value for jump I–II $= 2\cdot298$ (taken as 2·3 in formula).
Mean value for jump II–III $= 1\cdot627$
$1\cdot627 \times 2\cdot298 = 3\cdot74$ (taken as 3·8 in formula).
Mean value for jump III–IV $= 1\cdot435$
$1\cdot627 \times 2\cdot298 \times 1\cdot435 = 5\cdot37$ (taken as 5·4 in formula).

It will be seen at once that there is no evidence for jumps in tone which are simply related to one another. And, as has been stated earlier in this paper, in the absence of resonators there is no a priori reason for supposing that there would be a simple numerical relation.

§ 10. EFFECT OF SOUND ON PRODUCTION OF EDGE TONES

As has been mentioned in § 5, the whole edge-tone phenomenon occurs within the sound-sensitive range of the jet. It is of interest therefore to compare the vortex motion due to sound with that produced by edge tones, and to examine the effect of superimposing one on the other.

It has already been seen that the wave-length of the edge tones for a given frequency and velocity is in good agreement with that found for sensitive jets, table III. If now the development is considered, it was found in the former research* that for maximum development (an angular spreading of about 60° and this corresponds approximately with edge-tone formations) the following relation holds:

$$u/Ud^{\frac{1}{2}} = 0\cdot29,$$

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* Reference (2), p. 718.

where d is in mm., which, with the new convention adopted for λ, becomes

$$u/Ud^{\frac{1}{2}}=0{\cdot}37.$$

A glance at table 3 shows that u/U when $d=1$ mm. only reaches this value when U is about 300 cm./sec. Consequently, correspondence between edge-tone and sound-produced vortex motion is not to be expected below this velocity. This is well borne out by observations made at random, the first similarity in appearance being found for the following values:

Stage II, $h=1{\cdot}55$ cm., $n=164$ c./sec., $U=300$ cm./sec.
Stage III, $h=1{\cdot}89$ cm., $n=204$ c./sec., $U=329$ cm./sec.
Stage III, $h=2{\cdot}03$ cm., $n=189$ c./sec., $U=300$ cm./sec.

It is to be noted that in the above cases the intensity of the sound from the loudspeaker was such that it was easily audible, whereas when $U=300$ cm./sec. no edge tone can be heard. This important fact indicates that the vortex motion in edge tones, although only occurring with sound-sensitive jets, is nevertheless not entirely maintained by the sound emitted, a view which the writer favoured when he first took up this research.

The effect of sound upon the edge tones for velocities above 300 cm./sec. was examined in the following manner. The stream was given a fixed velocity, and the frequency of the loudspeaker at full strength was adjusted until the stream was most disturbed. The stroboscope was run at this frequency and then the wedge was slowly lowered into the stream until the frequency changed, i.e. the wedge controlled the frequency of the vortex motion. The results can be summarized as follows:

(*a*) *Stage I*: The loudspeaker never retained control during stage I whatever the values of h and U.

(*b*) *Stage II*: For velocities from 150 cm./sec. to 330 cm./sec. the loudspeaker prevents the formation of any stage except I. From $U=330$ onwards it ceases to control the whole of stage II. For instance the wedge controls stage II from $h=1{\cdot}00$ cm. downwards for $U=339$ cm./sec., from $h=1{\cdot}31$ cm. downwards for $U=358$ cm./sec., and from $h=1{\cdot}56$ cm. downwards for $U=482$ cm./sec.

(*c*) *Stage III*: The loudspeaker controls stage III up to $U=725$ cm./sec. Visual observation becomes difficult above this value, but at higher velocities beats are heard showing that the wedge does regain control when $U>1000$ cm./sec.

(*d*) *Stage IV*: The wedge never controls stage IV.

(*e*) It is possible to observe vortex motion superimposed on the edge-tone vortices, provided that the frequency is from four to five times that of the edge tone. Figure 9 of the plate illustrates this phenomenon for the case where $h=3{\cdot}5$ cm. and $U=127$ cm./sec., giving an edge tone for which $n=20{\cdot}5$ c./sec. (stage II). Superimposed are sound-produced vortices for which $n=102$ c./sec. It is interesting and important to note that the sound vortices grow in a perfectly normal manner* until they reach the region near the edge, and how, even afterwards, they still retain some of their features whilst forming part of the larger edge-tone vortices. This fact will be used later as evidence against the hypothesis that edge tones are due to disturbances starting from the orifice.

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* Cf. reference (2), plate 2, figure 5*F*.

(*f*) An interesting case occurs when $h = 4{\cdot}5$ cm. and $U = 182$ cm./sec. (stage III). The range of frequency of the loudspeaker controlling the vortex motion is from 46 to 230 c./sec. When $n = 136$ c./sec., however, the loudspeaker loses control and the vortices are superimposed on the edge-tone motion which is now able to maintain itself. When $n = 134$ c./sec. and $n = 138$ c./sec., and throughout the rest of the range, the loudspeaker controls the motion. Now this frequency was found to produce a marked minimum disturbance of the jet in the former research on sensitive jets.* It appears therefore that it may be the widening-out effect of the sound on the jet that makes its edge-tone formation impossible.

§ 11. EDGE TONES AND BEATS

As has been mentioned in § 10, when the velocity is high the effect of sound on stages II and III is to produce beats; the loudness increases with the amplitude of the impinging sound waves. The following are typical examples: (1) $U = 1200$ cm./sec. $h = 0{\cdot}75$ cm., stages I and III together giving $n_1 = 680$ c./sec. and $n_3 = 2580$. Lowering the loudspeaker frequency from 2580 c./sec. to 2500 c./sec. caused a beat note to rise from zero. Raising the frequency above 2580 did not produce any effect. (2) $U = 1660$ cm./sec. $h = 0{\cdot}57$ cm., stages I and II together giving $n_1 = 1270$ c./sec. and $n_2 = 2910$ c./sec. Raising the loudspeaker frequency from 2910 c./sec. to 5560 c./sec. caused a beat note to rise from zero.

§ 12. EFFECTS PRODUCED BY BEARDS

Obstructions placed in the immediate neighbourhood of the air stream between the orifice and edge are called by organ builders "beards"; they consist usually of pieces of wood, circular or oval in cross-section, held near the mouth of the pipe by being pinned through the "ears".† With a beard consisting of a glass photographic plate of length equal to that of the slit (2·36 cm.) at a height of about 2 mm. above the orifice, the following observations were made: $U = 262$ cm./sec.; $h = 2$ cm.; stage III. With the beard almost touching the stream it was deviated towards the beard and no oscillation was observable, but as it was pulled away first stage I appeared ($n = 45$ c./sec.), then stage II ($n = 105$ c./sec.), and finally stage III. If this was done very carefully the final stage was II, which is just possible (cf. figure 1). As the beard was pulled away the frequency increased slightly. Thus stage I can be brought back, after it has jumped to stage II or III, by interposing the beard, and the action of the latter appears to be simply that it deviates the stream towards itself in such a manner that the stream does not strike the edge centrally. A similar result can be obtained without the beard by moving the edge a little to one side: this has the effect of prolonging the lower stage as has been observed by

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* Cf. reference (2), table 1, p. 708.

† Cf. reference (13), p. 163.

Wachsmuth(7). The beard is most effective in deviating the stream when it is placed near the orifice and this is in accordance with organ building practice where it is used to bring back the prime from the octave(14).

When stage I occurred with stage III in the case already referred to (§ 8), it was found that the beard had the effect of stopping stage I rather than augmenting it, and this was the way in which stage III was isolated for the photograph, figure 8. It appears that when stage I occurs with a stream that it already disturbed by another vortex motion, it is much more sensitive to slight displacements.

§13. ACKNOWLEDGMENTS

The author's best thanks are due to Prof. E. N. da C. Andrade, F.R.S., for the facilities for this research and for his continued interest in it. Thanks are also due to Mr C. Jolliffe of Stowe School for many references especially on the subject of organ pipes.

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For references see page 520 of this volume.

THE MECHANISM OF EDGE-TONE PRODUCTION

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Received 10 *April* 1937. *Read* 25 *June* 1937

ABSTRACT. Former theories of the production of edge tones are reviewed and a new theory is put forward which accounts in a qualitative manner for the phenomena described in the preceding paper. The effect of the wake of a disturbance on the portion of the jet immediately following it is considered, and it is concluded that the compressibility and structure of the surrounding medium must be taken into account, and that, for low velocities, wake disturbance is the controlling factor, whilst for higher velocities the effect of the sound emitted must be taken into account. An attempt is made also to account for the differential sensitivity to frequency found in sensitive jets in a former research.

§ 1. FORMER THEORIES

Although edge tones had been discovered for some fifteen years, Helmholtz(15) did not discuss them except in connexion with an organ pipe. In this connexion he refers to his earlier paper on "The discontinuous motions of fluids"(16) and states that the bounding surfaces of the stream must be looked upon as vortical surfaces, i.e. surfaces "faced with a continuous stratum of vortical filaments or threadlike eddies. Such surfaces have a very unstable equilibrium." An example of this instability is the phenomenon of sensitive flames, and he makes a reference to Tyndall's experiments on gas jets. He continues: "This revolution into vortices takes place in the blade of air at the mouth of the pipe, where it strikes against the lip. From this place on it is resolved into vortices, and thus mixes with the surrounding oscillating air of the pipe, and accordingly as it streams inwards or outwards, it reinforces its inward or outward velocity, and hence acts as an accelerating force with a periodically alternating direction, which turns from one side to the other with great rapidity. Such a blade of air follows the transversal oscillations of the surrounding mass of air without sensible resistance."*

The view that the vortices form only at the edge is not borne out by experiment(4). Helmholtz also refers to Schneebeli's(17) mechanical explanation, which was that the air stream took the place of a solid reed. This view was also held by Cavaille Coll(18), Sonreck(19) and Hermann Smith(20). It is clear, however, that the tone-production is only explained if a pipe or other resonator is present, the oscillations in which cause the transverse motion of the air stream.

Lord Rayleigh in his *Theory of Sound*, 2nd edition (1896), does not attempt any explanation, but in connexion with the bird-call suggests that "when a symmetrical excrescence reaches the second plate, it is unable to pass the hole with freedom, and the disturbance is thrown back, probably with the velocity of sound, to the first plate, where it gives rise to a further disturbance, to grow in its turn during the progress of the jet" (p. 412).

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* Reference (15), p. 395.

The first attempt to account for the production of tones in the absence of any resonator was made by Wachsmuth(7). According to him, with a blunt edge no sound occurs until the distance of the edge from the orifice is such that the stream can spread on to both sides: the sharper the edge, the smaller this distance, but he does not explain why a minimum distance exists however sharp the wedge. When the stream spreads over the edge it must pass up one side first, and thus an asymmetry occurs which produces a periodicity in the velocity, through the alternate freeing and checking of the stream, and this must cause a pulsation in the air supply. That the stream starts to bend before the edge is reached is due to its behaving like a flexible bar, which buckles in the middle when it first strikes the edge. The bent portion travels up without returning to the vertical, since it is not a rigid body and the backwash (*Rückstau*) from it maintains the stream in a disturbed condition at a point below the edge. Wachsmuth adds that his researches did not decide whether the actual tone-production was due to the to-and-fro motion of the lower straight portion of the stream or to vibration of the wedge itself: he preferred the latter theory since, when h is large, the tone is heard near the wedge and not near the orifice.

With regard to the latter question, it can easily be shown that vibration of the wedge is not the cause of the tone, by holding the edge with the fingers, which, as Benton* has remarked, provide very efficient damping. No difference in tone-production occurs.

Wachsmuth did not justify his assumption that an air stream can be treated as a flexible rod and that it would break in the middle on striking an obstacle. He gave no physical explanation of the jumps in tone, and there is no evidence for the pulsation in the air supply.

The problem was next examined by König(9), who developed a hypothesis similar to that made by Lord Rayleigh in connexion with bird-calls. He pointed out that the jet could not be treated as a body with periods of its own, so that a simple resonance principle cannot be invoked, and he added that neither considerations of friction along the wedge nor of pendulation of the stream threw much light on the mechanism of tone-production. He assumed that when the edge was struck a sudden stoppage in the stream occurred and a compression wave travelled out in all directions with the velocity of sound. This would produce a disturbance at the orifice which would travel upwards with the velocity of the stream and create a new stoppage. If the velocity of sound in air is c, the period would be $h(c+U)/cU$, and with c very much greater than U the frequency n would be given by

$$n=\frac{U}{h}.$$

But this gives double the observed frequency. König therefore was forced to suppose that somehow the first compression produces a rarefaction at the orifice and he then obtained

$$n=\frac{1}{2}\frac{U}{h}.$$

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* Reference (6), p. 126.

He had to admit, however, that Göller's results(11), which he was using, showed that the factor was not ½ but between 0·4 and 0·5, and that for other intervals it became 1·0 and 1·5, and that his theory gave no account of this, neither did it explain why the tones do not commence with the highest audible note. He concludes by suggesting that since the velocity of sound is $(c-U)$ in the stream and c outside, this may cause pressure differences which might affect the tone.

Schmidtke(3) begins by asserting that the results of Wachsmuth and Göller show that n is proportional to U and inversely proportional to h and that the jumps in tone are octaves. This being so, König's formula can be written

$$\frac{2hn}{JU} \simeq 1,$$

where $J=1$ for the first interval, 2 for the second and so on. (The last column in table 2 on p. 501 of this volume shows the value of $2hn/JU$.) Schmidtke points out that König's derivation of the formula is unsatisfactory, and then attempts to make use of Kármán's vortex street. Such a street, he suggests, is set up along the sides of the wedge in stage I and between the orifice and wedge in later stages. Since he held that the frequency of the tones was equal to the number of vortices set free per second, it followed that in a Kármán street the same frequency could be produced again by moving the wedge a distance of $\lambda/2$; i.e. for the same frequency and velocity the difference between the wedge-distances must be constant. Schmidtke could not prove this with the results he had obtained for water jets since he did not succeed in getting more than one jump. He quotes, therefore, some values from a research by Rieth(12) with air jets, which support this conclusion. A table similar to that drawn up by Schmidtke but covering a much greater range of velocities has been given in table 1 of the preceding paper, and it can be seen that $(h_{m+1}-h_m)$ is approximately a constant, but it should be noted that the constant is not $\lambda/2$ but more nearly λ. A glance at figure 3 of that paper shows that although with respect to the vortex motion the wedge has moved only $\lambda/2$ each time, with respect to the orifice it has moved a distance λ, the vortex motion having moved away from the orifice by a distance $\lambda/2$. Further, on Schmidtke's theory, the product of n by the mean of $(h_{m+1}-h_m)$ ought to be constant and he had to admit that it was not. Schmidtke, however, concluded that a case had been made out for a Kármán street between the orifice and edge, but he did not attempt an explanation of its origin and did not provide any direct evidence of its existence.

Krüger(26) was the first to realize that a disturbance travelling up the jet would have a velocity u different from the stream-velocity U. He made the further suggestion that the jet has a natural wave-length λ_0 corresponding to its own tone ("jet tone") in the absence of the wedge. The oscillation of the stream would therefore be greatest when the edge-tone wave-length and jet-tone wave-length were the same. As h increases, the difference between it and λ_0 becomes greater, and the amplitude of the forced oscillations consequently smaller. When h approaches the value $2\lambda_0$, the wave-length jumps back to λ_0, corresponding to an octave jump in tone, and resonance again occurs. Krüger did not substantiate this hypothesis by comparison with experimental results. If this is done, the present research shows that the heights at which jumps in tone take place are not simple multiples of a fixed length, and further, the suggestion that the oscillations of the stream will become smaller as h approaches $2\lambda_0$ is the reverse of what actually occurs: the oscillations increase in amplitude as h increases in stage I until the jump occurs to stage II, and then the amplitude of stage II increases until the jump to stage III and so on. The use of a resonance principle by Krüger does not, therefore, seem to be justified, and there is no explanation of λ_0.

Benton(6) is another investigator who has claimed to show that a Kármán vortex system exists. He assumed that if the wedge were moved across the stream the point at which the tone disappeared would be a point on the path of the vortex centre. He measured the width b of this tonal boundary at different heights of the wedge and further assumed that h was equal to λ. He found that b/λ fell from 0·5 to 0·28 as the slit-width increased from 0·1 mm. to 1·88 mm. Instead of proceeding with wider slits, he assumed that this was a limiting value independent of the slit-width, and so concluded that for "very wide slits" b/λ approaches the Kármán value of 0·28. It happens that for $d=2$ mm. this ratio has a value close to Kármán's but for other widths it differs widely.* So that, even if Benton's assumptions are admitted as correct, he does not succeed in presenting any evidence for the Kármán vortex street, and, further, he gives no theory of its origin or of the jumps, since he has denied the occurrence of the latter (cf. § 3).

Richardson(8) while favouring the Kármán street theory, although providing no direct evidence for it, describes an experiment which indicates that the theory of a compression wave travelling backwards from the edge to the orifice with the velocity of sound is not correct. A second jet near the first one, but without a wedge, should have been affected by the sound wave, but no disturbance of any kind was observed. This experiment was made with water.

§ 2. THE KÁRMÁN VORTEX STREET

In view of the assumption by many writers that the conception of the Kármán street is applicable to fluid jets, an assumption which has led to the superficial claim that the phenomenon of edge tones and jet tones is thereby explained, and to the neglect of further research, it is important to consider this theory in greater detail.

Von Kármán considered the case of two parallel rows, of indefinite extent, of isolated, equal, point vortices in a fluid which was incompressible and without viscosity. He was then able to show that there was instability for infinitesimal disturbances unless $a/\lambda=0{\cdot}28$, where a is the distance between the rows. He concluded that this configuration was definitely stable, but, as Lamb(21) remarks, he did not prove this, and lately Schmieden(22) has shown that for certain finite disturbances it is certainly unstable.

It is clear that any application of this result to physics would have to be made with caution, and the experimental verification has never been satisfactory, even in the case of vortices at some distance in the wake of an obstacle⁽²³⁾. When gaseous jets are considered, the vortex rows cannot be of indefinite extent nor can the vortices be equal, and further, the fluid is not incompressible or free from viscosity. A priori, therefore, there is no reason for expecting to observe a constant ratio of a/λ and certainly no reason to suppose that this will be 0·28.

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* Reference (2), table 3.

The lack of evidence for the assumption of the Kármán street in the theory of edge tones has already been commented upon in § 1. In the case of jet tones which are produced in the absence of the wedge, Krüger and Schmidtke(24) claimed to have found the exact Kármán ratio using water. Four observations only are given, viz. 0·30, 0·27, 0·28 and 0·29 from which a triumphant mean of 0·285 is obtained. It may be concluded, therefore, that there is no reason for supposing that the constant Kármán ratio would occur in jets and that, in fact, it has never been observed.* Indeed it is remarkable that a mathematical theorem which neglects the compressibility of the medium should ever have been expected to account for the alternate compressions and rarefactions of which edge tones consist.

§ 3. THE PHYSICAL THEORY OF EDGE-TONE PRODUCTION

As was mentioned earlier, the present writer, after giving a theory of the action of sound on fluid jets, favoured the hypothesis that edge tones are maintained by the sounds travelling back to the orifice and producing a vortex formation similar to that in sensitive jets, and that, in some way, the edge stabilizes the motion. The sound has been shown to arise in the region where the vortex first begins to throw out a filament; this filament as it advances from $\theta=0$ to $\theta=3\pi$ (cf. § 4 of the preceding paper) entrains air, and it is the sudden pressure changes in this region † that result in the propagation of sound waves. Although this hypothesis is partly correct it fails to account for the following facts: (*a*) In some of the cases where it was found that vortex motion which was apparently identical with that due to the wedge could be produced by the loudspeaker alone, it was observed that the intensity of the sound from the loudspeaker had to be easily audible, whereas no audible edge tone occurred. (Cf. § 10 of the preceding paper.) The wedge therefore must do something more than just stabilize sound-produced vortex motion. (*b*) In a case such as that illustrated in figure 9 of the plate facing p. 498 it is impossible that an edge-tone vortex-formation with the wave-length shown could originate in disturbance at the orifice and not be affected by the superposition of vortices developed to the extent of those in figure 9. The only observable effect is the widening of the stream: the frequency is not altered. (The superimposed frequency was made to be a simple multiple of the edge tone in figure 9 merely to obtain a stationary stroboscopic view.) (*c*) Similarly it is difficult to see how a jet can give out two nearly pure tones simultaneously, if each is produced by vortices developed from a periodic disturbance propagated from the orifice.

In consequence of these facts it is necessary to examine the effect of interposing an obstacle in a jet of fluid. The easiest case to consider first is that in which the angle of the wedge is increased until it is 180°, i.e. the jet impinges normally on a flat plate (see figure 1 *a*). In this case it is evident that if the jet is deviated towards the right side, the surrounding fluid in the neighbourhood of A is displaced. If this displacement takes place sufficiently rapidly a local increase of pressure occurs at A, and this in dissipating itself reacts on the jet, deviating it towards the left; this deviation, in its turn, produces an excess pressure driving the jet back towards the right, and so an oscillatory motion is set up. Such motion is easily observed with a stroboscope: no developed vortex formation is seen, but undulations such as are shown in the illustration* are observed.

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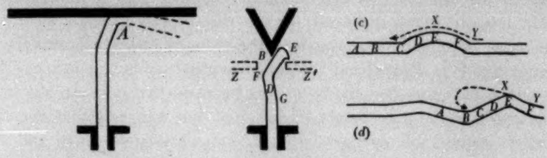
* Cf. reference (2), table 3.

† Reference (2), p. 730.

The nature of this type of disturbance of the surrounding air is a problem which has not yet been considered quantitatively. It is well known that if an obstacle is vibrated with very low frequency, there is a mass motion of the air from the front to the back and vice versa, and that pressure changes are negligible and can only be observed in the vicinity of the obstacle. At higher frequencies the reverse is the case: the mass motion becomes negligible and a pressure wave spreads to great distances with the velocity of sound. It is between these limits that the types of disturbance that are responsible for the oscillations producing edge tones occur.



(*a*) (*b*)

Figure 1.

Turning now to the wedge, it was found that with the velocity far below that at which oscillation commences, e.g. 82 cm./sec., it was possible to produce a vortex motion corresponding to that found in edge tones by moving the wedge slowly from side to side with an amplitude of about 1 mm. and a frequency of 1 or 2 per second. In this case the effect of such a slow motion is to cause the air to pass round the edge, from the side which the wedge is approaching to the opposite side. While this is done the stream is displaced: in figure 1 *b* for instance, if the wedge is moved to the left the air at B flows round the edge and moves the jet to the right; if this movement is large enough the portion of jet lower down at D may move to the left. The first appearance of the vortex filament may now occur at the exposed portion F, instead of at E.

If now the wedge is considered to be stationary, as it is in practice, the air at B can be displaced by the stream instead of the wedge. In the non-disturbed condition

* The fact that oscillation can be set up when a jet impinges on a flat plate or on a plate with a hole in it, as in the bird-call, or on other forms of obstacle, makes the effect of introducing an obstruction sideways towards the stream, as was done by Klug$^{(28)}$, very difficult to interpret since it may itself produce oscillation.

the stream bifurcates at the edge and passes half up one side of the wedge and half up the other. Now it has been shown that the whole of the edge-tone phenomena occur within the sound-sensitive range of the jet (see figure 5 of the preceding paper), so that a slight vibration of the apparatus, or a sound of the order of the minimum audibility of the human ear, is sufficient to produce a vortex which will pass up one side or the other.* The passage of the vortex along the side of the wedge displaces air, and it is suggested that in flowing back again in the wake of the vortex this air has sufficient momentum to deviate the stream towards the opposite side of the wedge. The momentum of the jet itself would merely cause it to return to the symmetrical position.

What occurs in the wake of an undulation in the surface of separation of two fluid media is a problem that has not so far been solved mathematically. Rayleigh's original calculations for a non-viscous fluid led to the result that a small sine-wave disturbance in the boundary of a jet should continue to grow in amplitude with time.† This, however, does not occur unless the velocity exceeds a certain value: below this value the crests flow over into the troughs and the boundary becomes straight once more.‡ Rosenhead(25) has attempted an extension of Rayleigh's treatment which indicates that the boundary between two non-viscous incompressible fluids would curl up in vortex-like shapes, but suggests that the distance λ between them cannot be derived without considering viscosity and diffusion. Rosenhead begins with a sine-wave disturbance already present in the boundary: his attempt to determine the result of a single undulation was not altogether satisfactory as it seemed to indicate a rupture of the surface; it seems possible that if he had represented the undulation by the displacement of several elementary vortices, a more definite result might have been obtained. This is a question of importance in the discussion of the mechanism of edge-tone production, since it seems clear that the wake of a vortex encountering the edge must exert a pressure on the following stream causing it to be deviated to the opposite side, see *FE*, figure 1*b*; and further that the motion of this portion may itself cause a reaction in the surrounding fluid which results in the portion *GF* being also displaced. In the absence of mathematical treatment a few qualitative general considerations can be made.

In figure 1*c*, *ABCDEF* represents a section through a laminar stream travelling towards the right with a small mean velocity U. *DEF* is an undulation travelling with velocity u. In discussing the reactions of the external air, it is legitimate to consider the undulation as stationary and the air as moving towards the left with velocity u. (Actually the relative velocity is less than u since the air is dragged along by the stream.) The particles at Y on being deflected at F exert a pressure on the surface tending to flatten it, and move upwards towards X. The excess of particles at X, tending to expand, exerts a pressure downwards on E and D and the flow is parallel to the surface as indicated by the arrow. The reaction on F, E and D is such as to produce a flattening and change of shape(25). Particles of the stream on the boundary get carried in the direction *FEDCB* since, owing to viscosity, there is no discontinuity of velocity, and thus the amplitude of the undulation gradually diminishes and the boundary becomes straight again. This is what is in fact observed; the undulations die out in a few wave-lengths.

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* Since the alternate position is adopted two vortices cannot pass the edge at the same instant. Cf. reference (2), p. 725.

† For references and criticism see reference (10), pp. 189–91.

‡ Reference (2), p. 710. Cf. figure 4A of plate I.

As the velocity is increased, however, a different type of flow must occur. This is represented in figure 1*d*. The particles at *Y* after deflection at *F* now have sufficient momentum to continue in their path when they reach *E* in spite of the excess pressure at *X* acting towards *E*. They therefore cannot enter the region *BCD* by the former path, but take a course indicated by the arrow, and this is followed by particles torn from the jet-surface; in other words a small filament extends outwards away from the stream and later bends inwards towards it, and thus the amplitude increases. The excess pressure at *X* can only be relieved in a finite time owing to the compressibility of the medium. No attempt appears to have been made to estimate this time quantitatively, but in the limit where the mass-motion is neglected it corresponds with Maxwell's "time of relaxation"(29). As the relative velocity increases, the reaction of the sudden formation of pressure at *X* will not affect the stream at the undulation *EDC* but later at *B*. The effect of this is to produce a deviation of the stream *ABC*. It is to be expected, therefore, that if a single-crest undulation is produced in a column of fluid it will be followed by a trough and possibly by further diminishing undulations, if the amplitude of the initial undulation is sufficiently great, since *ABC* may in its turn cause another crest. The amplitude will diminish since the particles condensed at *X* spread outwards in all directions and only a portion reacts on the stream: in this research the diminution of the amplitude was such that a crest was never followed by more than two others on the same side. Measurement of the wave-length is not easy, but the indications in the photographs are that it remains very nearly constant. This wave-length of the undulations following a disturbance travelling up a jet, in the absence of a wedge or other obstruction, may be called the *natural wave-length* λ_0 for the given velocity.

It seems physically possible therefore for a vortex-formation to occur in the jet before the edge is reached, although the actual cause of it is disturbance of the surrounding air at the edge. It is not necessary for the vortices to originate at the orifice, and this explains a feature of the cases illustrated in figure 3 of the plate facing p. 498: the velocity and frequency are constant and the vortex-formation is similar in each case except that it develops at a point farther from the orifice in each stage. If the vortices were initiated at the orifice, it would be difficult to account for this, but if the above hypothesis is correct it is clear that distance from the edge, and not distance from the orifice, is the deciding factor. It has already been pointed out in § 1 that this fact invalidates Schmidtke's hypothesis that $(h_{m+1}-h_m)$ would be equal to $\lambda/2$. This vortex formation occurring in the wake of a disturbance will be referred to as the *wake formation*.

Now although the wake formation is accompanied by pressure-changes in the surrounding medium, these may not at low velocities be sufficiently rapid to produce sound, but it must not be forgotten that when sound is produced there will be vortices formed which develop from the orifice in the manner described in a former paper(2), and the resultant formation will be a combination of the two. The velocity at which tones first become audible (and jets are of the same order of sensitivity as the human ear) was found to be about 500 cm./sec., and this was also found to be just below the velocity at which two notes of different frequency could be produced simultaneously. This can be accounted for on the above theory since two more or less distinct methods of vortex-production are now available, wake-production and sound-production. Figure 8 in the plate shows stage III with n equal to 800, and figure 7 shows the whole vortex formation moving from side to side in such a way as to produce the effect of stage I with n equal to 210. If stage III were entirely wake-produced it is difficult to believe that it would not be greatly modified by the wake of stage I. On the other hand, if stage III is maintained by sound waves affecting the sensitive region near the orifice these waves will be relatively independent of draughts in the wake of stage I. The edge, however, must still retain some wake effect on stage III sufficient to stabilize the tone. Stage I itself, at higher velocities, produces sound, but the wake formation is always the controlling factor (cf. § 10 of the preceding paper), and stage I is the only stage of which this is true, the other stages being due to a combination of a wake formation and a sound formation. It is therefore to be expected that stage I will be the only stage (above $U=500$ cm./sec.) that can occur simultaneously with one of the others. The sound is produced mainly by the to-and-fro motion of the jet at the edge, which is not modified appreciably by superimposed vortex motion as long as this is not greatly developed; cf. figure 8 of the previous paper.

§ 4. EXPLANATION OF FREQUENCY VARIATION AND DISCONTINUITIES

The physical processes underlying the variation of frequency with height of the wedge when the velocity is constant can be indicated with the help of the considerations given above.

Starting with $h=0$ there is no possibility of oscillation of the column, and any disturbances would not grow into a vortex producing an effective wake until they reached a point some distance up on the side of the wedge. Thus a minimum value h_0, below which no sound can be produced, must exist for each width of stream. This is well known from experiment and Benton found that $h_0 \propto d^{\frac{1}{2}}$: this is in agreement with another observation that was made, namely that when the velocity exceeded the Reynolds turbulence velocity, and the stream was therefore widened by vortex growth commencing at the orifice, the value of h_0 rose from 0·31 cm. to 0·34 cm. It was possible with h equal to 0·31 cm. and U equal to 3000 cm./sec. to hear no tone and then, on stopping the air pump, to hear the tone suddenly begin as the velocity dropped below the Reynolds value.

As h is increased, the position at which a vortex is formed on the side of the wedge approaches the edge.* This increases the effect of its wake disturbance at the edge, and this coupled with the decrease of velocity of the jet with distance from the orifice causes the amplitude of the oscillation to increase, accompanied by an increase in λ and therefore a decrease in frequency.

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* Compare figure 4 with figure 3 in the plate facing p. 498. In figure 3 a jump to stage II is imminent.

This increase in amplitude continues until the column is deflected through a very acute angle, as can be seen by examination of the plate. (All the stages in figure 3 are advanced developments, i.e. close to a jump to a higher stage. In figure 6, stage II is very close to a jump to stage III. Figure 8 is an example of vortex-formation at small amplitude, i.e. near a jump *down* to stage II if the velocity is decreased.) This deflection of the stream varies between a minimum of about 25° and a maximum of about 60°. As this deflection increases, it produces a wake disturbance itself, sufficient to deflect the stream to the opposite side, for instance, in figure 10*b* *FE* to the right is followed by *GF* to the left. As h is increased, the deflection of *GF* becomes such that the first vortex filament is thrown out at *F* instead of at *E*. The whole vortex formation then changes, since the vortices now reach a development represented by $\theta = \pi/2$ before encountering the edge. The effect of this appears to be to diminish the wave-length, and the frequency consequently jumps up. Further increase in h causes the amplitude and wave-length to increase as before (cf. table 2 on page 498, films 28 B and 27 F, where λ rises from 0·45 to 0·64 cm. on h being increased from 1 to 1·5 cm. while $U = 344$ cm. in stage II). Another point is then reached where the amplitude is such that a filament spreads out at a point still further from the edge and develops to $\theta = 3\pi/2$ before striking the edge. The vortex formation again changes and the frequency jumps once more corresponding to the change from stage II to stage III. The jump from stage III to stage IV is similar but no jump from stage IV is possible since after the vortex development represented approximately by $\theta = 3\pi$, the jet has a straight closed boundary and therefore cannot produce a wake disturbance of the kind considered in § 15.

It is reasonable to suppose that the edge-tone wave-lengths bear some relationship to the natural wave-length λ_0 for a given velocity. If it is supposed that these vary about λ_0 as a mean, this supposition is equivalent to expecting that the jet-tone curve would pass through the centre of the conical area occupied by the edge tones in figure 5, page 498. No values for the jet tones emitted by a 1-mm. jet are available and they are extremely difficult to determine: the maximum jet-width used by Kohlrausch(30) was 0·75 mm. and extrapolation from his graphs indicates that the jet tone is much lower than any edge tone. The author verified many of Kohlrausch's observations but found that two notes are produced, the higher one being the octave of the one measured by Kohlrausch, and for a 0·75-mm. jet-width these tones lie approximately in the centre of the conical area in figure 5 and about half way between the two extreme limits of sound sensitivity. If it is assumed that there is little difference between the jet tones for 0·75-mm. and 1-mm. jets, and that the octave note is the one corresponding to the wave-length λ_0, there is some support for the relationship expected. The author hopes to deal with the problem of jet tones in a further research.

The variation of frequency with the velocity of the stream when the height of the wedge is constant can be considered in a similar manner. Starting with the wedge at some fixed height, the first possibility of oscillation will occur when the velocity is such that any disturbance develops sufficiently to produce a vortex whose wake deviates the oncoming stream. Which of the four stages then sets in depends on the height: i.e. on the distance from the orifice. Once a stage is formed, increasing the velocity causes greater vortex growth and therefore greater wake-disturbance, but it seems that the resultant of this effect and the increased momentum of the jet is such as to keep λ constant although the amplitude increases. This rather remarkable fact, which is demonstrated by table 3 on p. 502, results in the frequency rising linearly with the velocity since $n = u/\lambda$ and varies as U/λ for large values of U. For values of U for which u/U is not constant the relation between n and U is no longer so closely linear.

It is possible, therefore, in a general qualitative way to account for the phenomena exhibited when a wedge is inserted into a jet of fluid. To attain quantitative results a detailed treatment involving the structure of the fluid is required, and so far this has not received attention in hydrodynamics; the difficulty has been avoided by taking either pv or pv^γ as constant; in other words the pressure changes considered are either very slow or very rapid in comparison with the molecular interchange of momentum.

§ 5. FACTS SUPPORTING THE PRESENT THEORY

It is clear that for velocities well below 500 cm./sec., for which the vortex formation is due entirely to wake disturbance, an obstruction such as zz' in figure 1 *b*, would interfere with the propagation of any disturbance in the surrounding air in the direction of the orifice. If, however, edge tones are maintained by a compression wave travelling back from the *edge* and causing a disturbance at the orifice, as was supposed by Wachsmuth, Rayleigh, König and others, the presence of zz' should not prevent the initiation of oscillation.

A brass plate containing a slit 2 mm. wide was placed in the position of zz', and the height of the wedge was made to be 3·5 cm. The first sign of oscillation as the velocity was increased from zero did not occur until $U = 200$ cm./sec. and then stage III began with a frequency slightly above the normal. Without the plate, oscillation starts when $U = 117$ cm./sec., stage II. Stage II, therefore, was prevented, and this was found to be the case even when the width of the slit in the plate was increased to 8 mm.

When $h = 0·5$ cm. the minimum velocity without the plate is 251 cm./sec.; with the plate this must be increased to 594 cm./sec. This corresponds to the elimination of stage I. The vortices are much smaller in this case (cf. figure 8 of the plate facing p. 498) and sound is also produced, so that in this case stage II is not prevented.

Stages III and IV are almost independent of conditions near the edge. For example it was found that if z and z' approach until they actually touch the wedge and are then moved down towards the edge, stages III and IV are not affected until z and z' approach within about half a millimetre of the edge. The oscillation then adopts the form illustrated in figure 1 *a*.

These facts are such as would be expected on the present theory, and the latter receives further support from the following considerations. If the wedge is replaced by a wire in the position of its edge the wire may not deviate the stream sufficiently to produce a large wake-disturbance, and it is possible that stage I, at least, might not be possible. This was confirmed by experiment. A wire of diameter 0·12 cm. was rigidly fixed at heights varying from 3·5 cm. down to 1·8 cm. Neither stage I nor stage II was possible. With the diameter reduced to 0·07 cm., only stage IV could be obtained, and the minimum velocity was approximately 320 cm./sec., which is the velocity at which a free jet becomes turbulent without any obstacle, so as to adopt the well-known wedge-shaped appearance. (Flickering appears at 150 cm./sec.) On the compression-wave theory these facts would again be difficult to account for, since the wire is a blunter object than the sharp edge of the wedge.

Another effect to be expected according to the present theory would be a change in frequency with angle of the wedge. If the wedge in figure 1 *b* is opened out until its angle is 180° as in figure 1 *a* the wake disturbance occurs under different conditions. The dissipation of excess pressure at A in figure 1 *a* in a more confined region would lead to the expectation that λ would increase, and that in consequence a decrease in frequency would occur. This is in agreement with experiment.

With U equal to 239 cm./sec. and h equal to 1·07 cm. in stage I it was found that the frequency fell from 66 c./sec. to 61 c./sec. when the wedge angle changed from 20° to 90°. Richardson also found a decrease when the wedge angle increased from 5° to 30°.*

The important role played by movement of the surrounding air accounts for the ease with which the frequency of edge tones is controlled by any form of resonator near the edge, a fact noticed by Wachsmuth(7) and familiar in musical instruments.

§6. APPLICATION OF THE THEORY TO SENSITIVE JETS

The effect produced by the wake of a vortex on the stream which has had to be considered in this research obviously has an important bearing on the problem of explaining why jets exhibit a sensitivity to sound which varies with the frequency. It has been necessary to suppose that a vortex passing up a jet will be followed by an undulation of a definite wave-length owing to the reaction of the surrounding air. If then the impressed sound is of such a frequency as to produce alternate vortices having this wave-length, the undulation and consequent vortex-growth will be greatly enhanced. On the other hand if the frequency is such that the wave-length is just half the natural or wake wave-length, it seems likely that for this frequency the jet would appear almost undisturbed. Examination of the results obtained for illuminated coal gas supports this view,† but there are many subsidiary maxima and minima and the subject requires further investigation. The hypothesis that the reaction of the surrounding air has a controlling influence on the wake wave-length is rendered more acceptable when it is recalled that the frequencies of maximum and minimum disturbance are independent of the shape and size of the jet.

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* Reference (8), figure 6.

† Reference (10), figure 9.

§7. CONCLUSION

The detailed examination of edge tones described has shown that former theories cannot adequately account for all the phenomena observed, and that the evidence supporting the hypothesis of a Kármán vortex street, and of jumps in tone bearing a simple numerical relationship, is not reliable.

The effect of a disturbance travelling up one side of a jet is considered, and it is concluded that this produces in the surrounding air a sudden local increase of pressure, which in dissipating itself reacts on the jet in the rear of the disturbance, deviating it towards the opposite side. This deviation, if its amplitude is sufficient, may itself be followed by wake disturbance causing the jet to be deflected once more, and thus undulation may occur in portions of the jet which have not yet reached the edge. The fact that all the edge-tone phenomena occur within the sound-sensitive velocity-range of the jet has been made use of to explain the initiation of the original disturbance. Above a certain minimum velocity such disturbances develop into vortices on being deflected by the edge. According to the amplitude of the resulting wake disturbance (and this can be increased by augmenting the velocity or the wedge-distance), vortex motion may begin at the first, second or third crest of the following undulations. This results in four vortex stages, and in jumps in tone. The periodic increases of pressure near the edge produce the edge tones. For high velocities, the effect of sound on the vortex formation in the jet, described in a former paper, must be taken into account as well as the wake disturbance. In general the vortex motion is the resultant of both causes, but in certain cases they can act separately, and then two different vortex formations are produced simultaneously and these result in two tones of different pitch being heard.

In sensitive jets both causes are active and it is suggested that in the resultant complex reaction is to be found the origin of the differential sensitivity to sound of varying frequency.

§8. ACKNOWLEDGMENTS

The author's best thanks are due to Prof. E. N. da C. Andrade, F.R.S., for the facilities for this research and for his continued interest in it. The author is also indebted to Dr R. E. Gibbs for help in matching jet-tone frequencies.

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THE PRODUCTION OF CHLADNI FIGURES BY MEANS OF SOLID CARBON DIOXIDE. PART 1: BARS AND OTHER METAL BODIES

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Received 31 *March* 1937. *Read, with demonstration,* 11 *June* 1937

ABSTRACT. Chladni figures can be very readily produced by means of solid carbon dioxide: some photographs of results obtained on metal objects of various shapes are shown. The frequencies of the vibrations excited in objects of low fundamental tone usually lie between about 1000 and 4000. The theoretical implications of this fact are considered.

§1. INTRODUCTION

A GENERAL theory of the production of pure loud notes from metal bodies by means of solid carbon dioxide has been given previously(1), and the circumstances which led to the discovery have also been recorded(2). The production of Chladni figures, more especially of the nodal lines that may be produced on metal bars, has been undertaken in a further study of the phenomenon. At the same time it has been established that the method of excitation provides a rapid and simple way of obtaining these figures on bodies both of regular and of irregular shape.

By means of these overtones, the limits of frequency within which the carbon-dioxide method of excitation is effective can be estimated with considerable accuracy. It appears that this preferred range depends relatively little upon the size, shape, mass, material or temperature of the excited metal. Conversely, a knowledge of the preferred range enables bodies of suitable dimensions to be chosen on which to produce Chladni figures corresponding to given overtones. The observations that are recorded below serve therefore two purposes. The one concerns the theoretical interpretation of the excitation phenomenon; the other a new method of obtaining Chladni figures that may be useful in the future.

§2. TECHNIQUE

The following points of technique, some of which have been mentioned previously, are important for producing effective vibrations.

(1) The solid carbon dioxide used must be of the high-density "ice" variety. I am indebted to Imperial Chemical Industries Ltd., for kindly supplying the solid carbon dioxide known as "Drikold" which was used in the present investigation.

(2) The area of contact between the metal and solid carbon dioxide must be small, and the pressure of application light. Figure 1 and the inset of figure 8 show pointed pieces of carbon dioxide which are suitable for purposes of excitation. It does not appear to be possible to substitute a mechanical device for the hand, and the skill of the operator in sensing the onset of vibration, the amplitude of which grows with remarkable rapidity, increases with practice. The point of application of the solid carbon dioxide (at or near an anti-node) may be either on the upper or the lower surface of the bar; for producing sand patterns it is often convenient to excite from below.

(3) The atmosphere should be dry. It was originally stated (1) that humidity did not affect the production of vibrations. This conclusion was based on observations made on a brass bar which vibrated so readily in the free-free fundamental mode of 2000 c./sec. that the difficulties subsequently encountered in moist weather with other vibrators were not anticipated. These may be partially overcome by warming the bars before use, and by sprinkling dried sand on to the cleaned surface at the last moment before excitation. Moisture from the air formed on the surface of the solid carbon dioxide cannot however be avoided; and when one is investigating the higher tones of the larger bars, especially if their vibration frequencies lie above or below those which are most easily excited by the solid carbon dioxide, it is well to experiment on a dry day. It is also sometimes desirable to discard a piece of carbon dioxide, if it appears sugary or breaks up easily, in favour of a piece broken by means of hammer and chisel from another part of the solid carbon-dioxide block. This last observation is of theoretical as well as of practical importance.

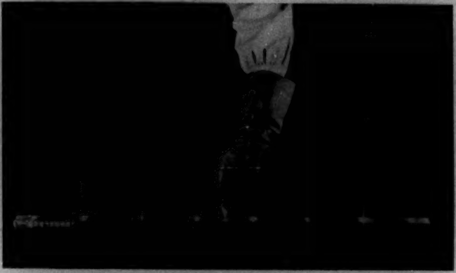

Figure 1. Production of Chladni nodal lines by means of solid carbon dioxide. Frequency, 1317 c./sec.

§ 3. FREQUENCIES OF VIBRATIONS EXCITED BY SOLID CARBON DIOXIDE

Provided that the fundamental of a metal object is high enough, that is to say about 1000 c./sec., this will be excited by means of solid carbon dioxide; it has been found possible to produce the two nodal lines on bars vibrating in the free-free manner up to 7000 c./sec. and to detect notes up to much higher frequencies.* The observations that have been made on objects of low fundamental are described below.

Brass bars of varying length and thickness. Figures 2 and 3, together with the data given in tables 1 and 2, illustrate the fact that the overtones that may be excited by means of solid carbon dioxide become progressively higher as the fundamental becomes lower. This latter varies inversely as the length squared in each of the series of bars of figure 2, and directly as the thicknesses of the brass bars shown in figure 3. It will be noted that all the frequencies lie between 1000 and 4325.

Table 1. Brass bars of varying length

Thickness, 1·27 cm. Thickness, 0·9 cm.

Length (cm.)	Tone*	Frequency		Length (cm.)	Tone*	Frequency	
		Excited	Fundamental (first tone, 2 nodal lines)			Excited	Fundamental
11·5	1†	3358	3358	11·5	1†	2156	2156
15·0	1†	1964	1964	15·0	1†	1263	1263
22·9	2†	2301	836	17·9	2†	2381	860
30·0	2	1298	469	20·2	2	1876	683
	3†	2523	"		3†	3700	"
				30·8	3	1588	300
					4†	2638	"

* Rayleigh notation. † See figure 2.

Table 2. Bars of varying thickness

Length, 60·45 cm.

Thickness (cm.)	Fundamental (to nearest whole number)	Tones excited*	Frequencies†
1·302	121	4–7	1098, **1630**‡, 2266, 2977
0·612	57	6–10	(1011) 1476, **1892**, **2328**‡, 2875
0·325	32	8–15, 17	(1010) 1280, 1560, **1880**‡, **2260**, 2504, 2950, 3400, 4325
0·624§	65	6–10	(1211) 1568, **2080**, **2500**, 3005‡

* Add one to obtain number of nodal lines. † The frequencies most usually obtained are in black type; brackets denote chattering. ‡ See figure 3. § Copper.

Metal objects of varying material, dimensions and temperature. In order to avoid giving lengthy tables, the essential details of a number of observations have been collected in figure 4. The frequencies of each tone excited are plotted on the right. A list of the objects excited, together with notes giving the main purposes of the various observations and the fundamentals are shown in the columns on the left.

Summary of results. A glance at figure 4 is sufficient to show that the range of frequencies that can be excited by means of solid carbon dioxide is remarkably definite, and does not vary very much from object to object. The results for the first

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* Frequencies were determined by means of a mains-operated calibrated valve oscillator, the property of the Augustus and Alice Waller Memorial Trust.

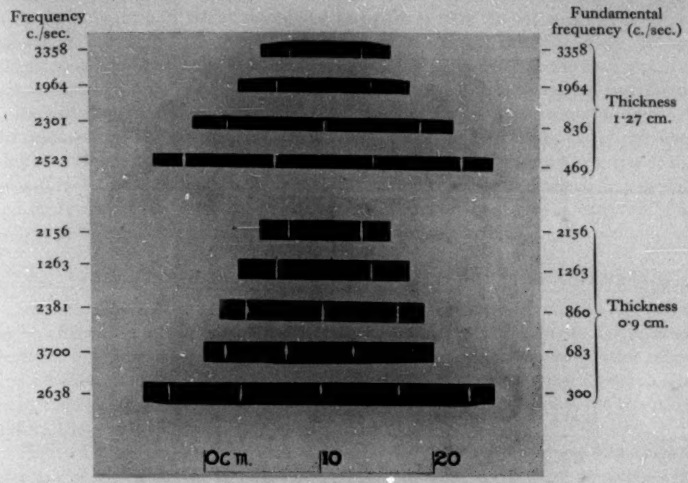
Frequency c./sec.
3358
1964
2301
2523
2156
1263
2381
3700
2638
Fundamental frequency (c./sec.)
3358
1964
836
469
Thickness 1·27 cm.
2156
1263
860
683
300
Thickness 0·9 cm.
0 cm.
10
20

Figure 2. Varying length.

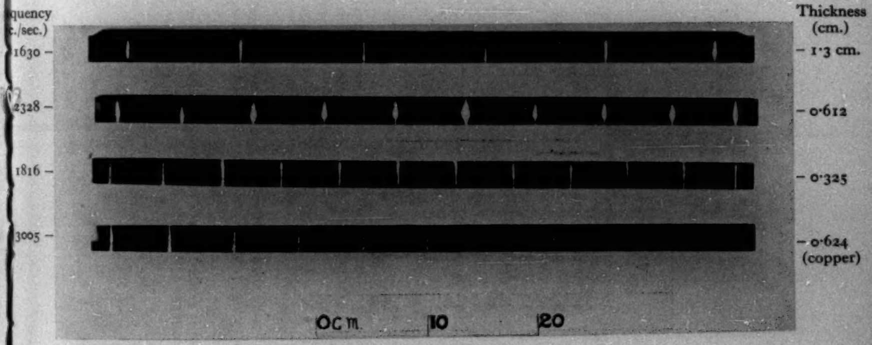
quency
c./sec.)
1630
2328
1816
3005
Thickness (cm.)
1·3 cm.
0·612
0·325
0·624 (copper)
0 cm.
10
20

Figure 3. Varying thickness.

	Vibrating object	Notes	Fundamental (first tone)	Tones excited
1	Copper bar	60·7 × 1·27 × 1·27 cm.	130	4–8
2	Mild steel bar	K = 0·9, 0·1	177	3–6
3	Copper bar	44·8 × 1·27 × 1·27	206	3–5
4	German silver bar	K = 0·9, 0·07	198	3–5
5	Brass bar, figure 1	m = 3·29 kg.	71	5–11
6	Aluminium bar	120·8 × 1·27 × 1·27	43	7–12
7	,,	l = 122. Diameter = 1·27	38	7–13
8	Mild steel bar	92·5 × 1·27 × 1·27	78	5–8
9	Brass bar	l = 91·35. Diameter = 1·27	84	5–8
10	,,	42·5 × 1·27 × 1·27	206	3–6
11	,,	20° C.	50	7–12
	,,	150° C.	48·5	7–12
12	,,	20° C.	21	10–20
	,,	150° C.	20	9–19
13	Narrow rods	Diameter = 4 to 6 mm.	—	Misc.
14	Brass plate	Diameter = 13 cm.	—	,,
15	,,	Diameter = 20 cm.	—	,,
16	,,	Diameter = 30 cm.	—	,,

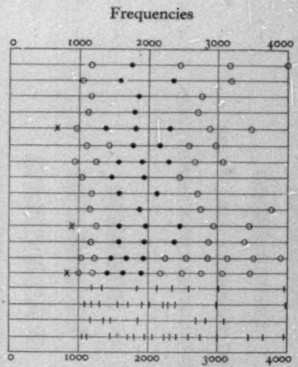

Figure 4. Frequencies of vibrations excited by solid carbon dioxide. K, thermal conductivity; •, most usual frequencies; ×, accompanied by chattering; |, miscellaneous overtones. The frequencies, N_1, given in the fourth column were calculated by means of the relation

$$N_1 = N_n\,9{\cdot}061/(2n+1)^2.$$

The tones excited in bars of circular cross-section were inferred from the ratios of the experimental frequencies which approximate to the squares of the odd numbers.

four bars show that a change of conductivity from 0·9 to 0·07 makes no detectable change in this range. The range is definitely lower for the massive fifth bar (938–3468), a photograph of which was given in figure 1, than for the small rods (1146–>4000) or brass plates (1070–>4000), 3 mm. thick (see also figure 9). It was difficult to establish any change due to temperature variation, but the final observations undertaken on a brass bar, no. 12, of particularly low fundamental frequency, 21, showed that the range was a little lower when the bar was heated to 150° C.* The intensity of the vibrations is often very great for the heated bars, provided always that the temperature is not sufficient to impair the vibrating properties of the metal. The latter is very important; it is, for example, easier to produce figures with hard brass than with annealed pure copper in spite of its high conductivity. The theoretical significance of these results will be considered in § 5.

§ 4. VIBRATIONS OF METAL OBJECTS OF IRREGULAR SHAPE

Excitation by means of solid carbon dioxide is very intense, and the fact that it can be effected at any point of the metal surface makes it possible to excite single overtones in objects of irregular shape which emit but a jangle of sound when struck with a hammer. A few illustrations of the possibilities of studying resonances by the method are given in figures 5 to 8. Incidentally the frequencies of the vibrations confirm the results of the previous paragraph.

Figure 5 (triangle) gives an idea of how far the ordinary transverse vibrations in the plane of the thickness are affected by breadth, while figure 6 (wedge) shows the manner of vibration when the thickness varies (from approximately zero to 8 mm.). The vibration frequencies of the triangle are from 7 to 10 per cent greater than those of the bar from which it was cut, and the nodal lines are very slightly displaced towards the base. The frequencies of the wedge are very roughly double those of the parent bar, and the adjustment of nodal distances to varying thickness and the large displacements of the nodal lines towards the thin end of the wedge will be noted.

The familiar Trevelyan rocker is shown, as it vibrated with and without its handle, in figure 8; these elastic vibrations are of course much higher than the gravity vibrations of the bar when it is rocking as a whole about its two ridges, and the figure is of interest in connexion with recent discussion concerning this ancient rocker(3).

Figure 7 shows the nodal lines produced on some spanners and a chisel, and suggests the possibility of studying resonances in pieces of machinery. The vibrations of large pieces could be investigated by means of small-scale models.

§ 5. MECHANISM OF PRODUCTION OF VIBRATIONS BY MEANS OF SOLID CARBON DIOXIDE

The production of vibrations by means of solid carbon dioxide, the temperature of which is at about −80° C., depends upon the sublimation which occurs when it touches the metal in the process. A large quantity of gas is produced, as has been

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* The slight shift of the frequencies that will be noticed in figure 4 for the heated bars is of course due to the temperature-diminution in Young's modulus.

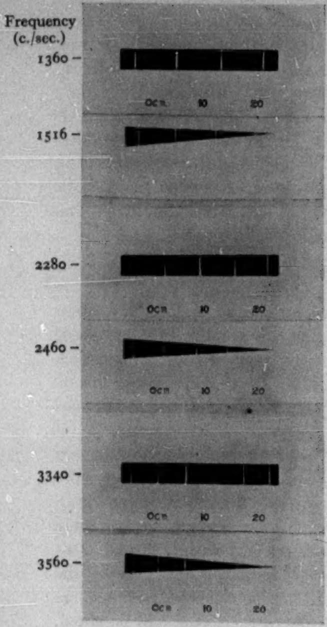
Frequency (c./sec.)
1360
1516
2280
2460
3340
3560
0cm 10 20

Figure 5. Bar and triangle. Thickness 6·84 mm.

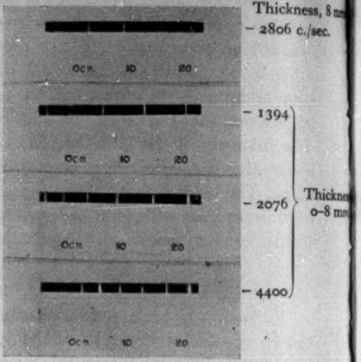
Thickness, 8 mm
2806 c./sec.
1394
2076
4400
Thickness 0–8 mm
0cm 10 20

Figure 6. Bar and wedge.

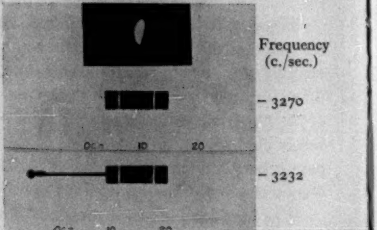
Frequency (c./sec.)
3270
3232
0cm 10 20

Figure 8. Trevelyan rocker (inset solid carbon dioxide).

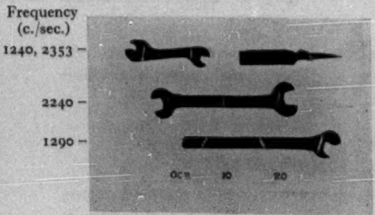
Frequency (c./sec.)
1240, 2353
2240
1290
0cm 10 20

Figure 7. Spanners and chisel.

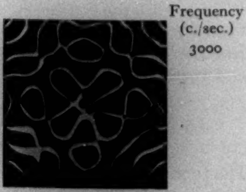
Frequency (c./sec.)
3000

Figure 9. Plate.

Figures 5–9. Study of vibrations of metal objects by means of Chladni figures produced by solid carbon dioxide.

shown by means of a Foucault-Toepler or Schlieren photograph(4), the pressure of which is most obvious in the experiments made with mercury(1).

The experimental results that have been summarized in § 4 can be explained by supposing that the main impulse depends upon the irresistible molecular forces of sublimation which are operative at the moment of contact. Each impulse lasts only for a small fraction of the total period and is given except at the beginning, while the vibrating object is at one extreme of its swing. The localized pressure is then very great as compared with that which exists during the rest of the vibration.

It is of interest to consider the relation between the mean free path of the CO_2 molecule, which is about $3{\cdot}9 \times 10^{-6}$ cm. at normal temperature and pressure, and the amplitudes of vibration. Andrade and Smith(5) have investigated the latter in connexion with the production of Chladni figures. Thus the motion at an antinode of the vibrating surface may be represented by $a \sin nt$, the maximum acceleration amounting to an^2. In order that figures may be produced on a bar, an^2 must be greater than g, or a must be greater than $g/4\pi^2N^2 > 25/N^2$, where N is the frequency of vibration. The frequency of vibration corresponding to an amplitude of vibration of $3{\cdot}9 \times 10^{-6}$ cm. just sufficient to produce motion of the sand under favourable conditions would be 2530. The vibrations being intense, at any rate at the higher frequencies, the amplitudes are no doubt considerably greater than these minimum values.

The mean free path cannot of course be estimated accurately. At the first moment of sublimation while the main impulse is occurring, it should be equal to about $p^{-1}.3{\cdot}9.10^{-6}\sqrt{(193/273)}$ cm., where p is possibly many atmospheres; but half a period later, when the vibrating object is at the other extreme of its swing, if the pressure is nearly atmospheric and the temperature not much below that of the room, the mean free path will not differ greatly from $3{\cdot}9 \times 10^{-6}$ cm. It is probable therefore that the upper limit of frequency that can be obtained with the carbon-dioxide method of excitation depends upon the vibration amplitude becoming comparable to the mean free path, and the impulse lasting too long in relation to the period to be effective.* The lower limit of frequencies is imposed by the increase in the chattering which is no doubt connected with the larger amplitudes of vibration.

It is evidently sufficient to have a material of relatively low thermal conductivity in order to produce enough sublimation to separate the two surfaces, and loud notes have been produced in a quartz bar cut from a large crystal, the conductivity of which is 0·06 or 0·03 according to direction(1). At the same time the production of gas is essential and no sound can be produced from insulators. Incidentally this provides a convenient way of distinguishing quartz from glass lenses since the former only, emit a rattle when touched with the carbon dioxide.

In the case of heated metals the impulses are more intense and the mean free path greater, so that the slight decrease of both the upper and lower limits of frequencies is also accounted for by the theory proposed. It might be possible to investigate this matter further with some alloy for which the internal damping remains small at high temperatures$^{(6)}$. One of the difficulties of producing maintained vibrations at higher temperatures is, however, that the shape of the solid carbon dioxide alters rapidly on account of the increased rate of sublimation.

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* The theory suggested experimenting with a very narrow, thin, long strip of brass ($1{\cdot}276 \times 0{\cdot}333 \times 86{\cdot}64$ cm.) and exciting it near one end. In such a case the range of frequencies excited should be higher. Clear nodal lines were obtained for all tones from the 15th to the 29th corresponding to frequencies ranging from 1690 to 6000. The fundamental can be calculated with accuracy and is found to be 15·61.

§ 6. CONCLUSION

The production of overtones in metal bodies by means of solid carbon dioxide has enabled the mechanism of the production of vibrations by this method to be studied in considerable detail. At the same time it has become apparent that solid carbon dioxide provides a peculiarly simple and effective method of obtaining Chladni figures. Powerful excitation can be immediately produced and maintained for some seconds at any point of either plane or curved metal surfaces, and it is possible by this means to study the resonances of objects of irregular shape.

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DISCUSSION

Dr O. Kantorowicz. I should like to ask whether it is possible to control the mode of vibration of a body, if this body has several possible modes in the frequency-range available. Does the author consider the method a suitable one for estimating the damping-capacity of metals, or does damping by sound-radiation mask the effect of internal damping so as to make its observation impossible? Even a rough method would be quite valuable.

Mr J. H. Awbery asked why the author expected to find a simple relation between the mean free path of carbon dioxide and the amplitude of vibration of the metal. He pointed out that in any event air would be mixed with the carbon dioxide. He suggested that local stresses might be set up in the metal as a result of contraction and expansion with changes of temperature.

Mr H. R. Calvert asked whether the author had tried ammonium chloride and other substances which sublimate under attainable conditions.

Author's reply. In reply to Dr Kantorowicz: The desired partials can be obtained by using very hard-pointed pieces of solid carbon dioxide for the higher notes and blunter pieces for the lower notes, the vibrating object being suspended from, or supported at, two nodal positions. The method of measuring the vibration-damping has been described in a previous paper$^{(6)}$; the air resistance can be neglected to a first approximation. Vibration-damping is probably connected with damping-capacity (as defined by Föppl) though the latter deals with conditions outside the elastic limit.

In reply to Mr Calvert: Vibrations have been produced in heated metals by means of a number of substances which either sublime, or boil, or decompose, with the evolution of gas(2). I did not succeed in detecting the vibrations when using ammonium chloride. The notes produced are feeble and transitory, and the phenomenon, except in the case of solid carbon dioxide, would not be noticed unless looked for.

In reply to Mr Awbery: The experiments just quoted, together with the fact that vibrations cannot be produced in the absence of evolved gas, show that radiation pressure due to the presence of air does not play any detectable part in the production of the vibrations. Nor do I think that local stresses are responsible, since the contact is so slight and the fall in temperature of the metal small. On the other hand the pressure produced by the carbon-dioxide gas is very obvious. The theory developed in connexion with the amplitude of vibration and mean free path of the carbon-dioxide molecule offers some explanation of the fact that the range of frequencies that can be obtained is so definite and varies so little from metal to metal. Longitudinal vibrations also have been produced(1), and further experiments with these might reveal the existence of higher zones of excitable vibrations.

ULTRA-VIOLET BAND-SYSTEMS OF GeCl AND GeBr

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Received 26 *May* 1937. *Read in title* 11 *June* 1937

ABSTRACT. Band-systems of GeCl and GeBr are developed in the regions λ3202–λ2847 and λ3260–λ2946 respectively in heavy-current tube-discharges through continuous flows of $GeCl_4$ and $GeBr_4$ vapours. Each consists of two subsystems of bands degraded towards shorter wave-lengths, the heads being represented approximately by

$$\text{GeCl: } \nu=\left\{\begin{matrix}33992\cdot2\\33017\cdot2\end{matrix}\right\}+(526\cdot6u'-0\cdot3u'^2)-(408\cdot4u''-1\cdot6u''^2),$$

$$\text{GeBr: } \nu=\left\{\begin{matrix}33413\cdot4\\32263\cdot4\end{matrix}\right\}+(383\cdot7u'-0\cdot7u'^2)-(296\cdot6u''-0\cdot9u''^2),$$

where $u=v+\frac{1}{2}$. The systems are probably $^2\Sigma\rightarrow{}^2\Pi$, the lower states, with electronic intervals 975 and 1150 cm.$^{-1}$ respectively, being the ground states of GeCl and GeBr. The electronic intervals $\delta\nu_e$, the upper state energies (system-origins) ν_e, and the vibrational coefficients ω_e and $x_e\omega_e$ for both electronic states are compared with those of band-systems of other monohalides of group-IV (*b*) elements. With increasing atomic number and mass of either atom (group-IV (*b*) or halogen) the expected trend is observed in each case, namely an increase in $\delta\nu_e$, and decreases in ν_e, ω_e and $x_e\omega_e$, except for $\delta\nu_e$ in SiBr and the Pb monohalides; the apparent anomalies are discussed.

§ 1. INTRODUCTION

ALTHOUGH a large number of investigations have been made of the band spectra of diatomic fluorides, chlorides and bromides of the group-IV (*b*) elements silicon, tin and lead, the results for the group as a whole are somewhat fragmentary and give apparently conflicting indications of the nature of the ground states. The ground states of the atoms Si, Ge, Sn and Pb are $ns^2np^2\,{}^3P$ with $n=3$, 4, 5 and 6 respectively, and those of F, Cl and Br are $ns^2np^4\,{}^2P_{\text{inv.}}$ with $n=2$, 3 and 4 respectively, the inner electrons being omitted in each case. From these states a $^2\Pi$ ground state may be expected for the monohalides$^{(1,2)}$, though $^2\Sigma$ also is possible. It will be well to review briefly the results of observations so far recorded.

For SnCl two ultra-violet band-systems, with 0 → 0 bands near λλ3198, 2973 A. and λλ3761, 3487 A., have been observed in emission$^{(3,4)}$ and assigned to transitions $^2\Sigma\rightarrow{}^2\Pi$ and $^2\Delta\rightarrow{}^2\Pi$ respectively, the lower state $^2\Pi$ with an electronic separation of 2360 cm.$^{-1}$ being common to the two systems. That this is the ground state of SnCl is suggested by a recent observation of the former system in the fluorescence of $SnCl_2$ vapour with ultra-violet excitation$^{(5)}$.

For SiCl three emission systems B → X, C → X and D → X, having 0 → 0 bands near λλ 2942, 2924 A., λλ 2436, 2424 A. and λλ 2232, 2221 A. respectively, have been analysed(6); they, too, have a common doublet lower state, which has an electronic separation of 207·9 cm.⁻¹ and appears, from its analogy to the lower state of SnCl, to be a $^2\Pi$ ground state.

In the case of the SiF emission spectrum the earlier vibrational analysis(7) has recently been revised and extended(2). Three systems, with 0 → 0 bands near λλ4270, 4241 A., λλ2893, 2880 A. and λλ2539, 2529 A., have been attributed to transitions $A\,^2\Pi \rightarrow X\,^2\Pi$, $B\,^2\Sigma \rightarrow X\,^2\Pi$ and $C\,^2\Sigma \rightarrow X\,^2\Pi$ respectively. The common lower $^2\Pi$ state is regarded as the ground state and has an electronic interval of 161 cm.⁻¹ A revision of the partial analysis of the rotational structure of the 3 → 3 band λ4368, of the first of these systems, has been reported(8).

The $^2\Pi$ lower states of the above three emitters, then, have electronic intervals which increase, as would be expected, in going from SiF to SiCl and from SiCl to SnCl; they are probably the ground states although there are no absorption observations to put the matter beyond doubt.

The analyses of the known band systems (or subsystems) of PbF, PbCl and PbBr indicate a single electronic level, such as $^2\Sigma$, $^2\Pi_{\frac{1}{2}}$ or $^2\Pi_{1\frac{1}{2}}$ but not a complete $^2\Pi$, in the ground state of each. The PbF system occupies the region λ4110–λ5277 (0 → 0 band at λ4441·1) and has been observed in emission(9) and in absorption(1). The PbCl system in the region λ4108–λ5170 (0 → 0 band at λ4579·6) has been observed in emission(9), in absorption(1, 9) and in fluorescence of $PbCl_2$ vapour with ultra-violet excitation(10). The PbBr system, which extends from λ4482 to λ5320 (0 → 0 band at λ4793·3), has been observed in absorption(1) and in fluorescence of $PbBr_2$ vapour with ultra-violet excitation(11). Only in these three cases is there such abundant proof that the lower state is actually the ground state. The electronic interval in a $^2\Pi$ ground state of each of these molecules would be expected to be much larger than that of SnCl; for example, it has been estimated(1) as 7000 cm.⁻¹ for PbCl. This implies that if the observed PbCl bands form the *less* refrangible subsystem of a doublet such as $^2\Sigma \rightleftarrows {}^2\Pi$, the missing subsystem would be very much more intense in absorption and very favourably situated for observation in the near ultra-violet. No bands are observed here, however. On the other hand, if the observed PbCl bands form the *more* refrangible subsystem, the missing subsystem would be very much weaker in absorption, and less favourably placed for observation in the extreme red and near infra-red. A search in this region for PbCl bands in emission from a heavy-current discharge tube might be worth attempting.

For SiBr, the only other emitter for which data are available, a system occurs in the region λ3233–λ2875, and the analysis(12) indicates an apparently single electronic level in the lower state, although comparison with SiF and SiCl (and with the emitters discussed in the present paper) would suggest a $^2\Pi$ state with an interval of 350–450 cm.⁻¹ The emission band spectrum of SnBr has also been observed(13) but no data and analysis have been published.

In the absence of any rotational analysis other than that of SiF(8), vibrational analyses of the band-systems of the remaining halides SnF, SnBr, GeF, GeCl and GeBr would seem to be the most promising means of gaining further insight into the nature of the ground states of the subgroup. Investigations of the spectra of the last two of these emitters, the results of which have already been announced in a preliminary note(14), are described in the following pages. In view of the apparently anomalous result (noted above) for SiBr, and the lack of data for SnBr, similar investigations have been made of these two emitters and will be described in a later paper(15); the result for SiBr has already been given in the preliminary note.

During the writing of the present paper it has become possible to include CCl in this discussion. A prominent cluster of band-heads near λ2788 in the uncondensed discharge through carbon tetrachloride vapour has been known for some time(16) but has not been interpreted until quite recently(17); it forms the strong part (0 → 0 and 1 → 1 bands) of a $^2\Sigma \rightarrow {}^2\Pi$ system of CCl, in which the lower state has an electronic separation of 136 cm.$^{-1}$

§ 2. EXPERIMENTAL

The sources used for the development of the GeCl and GeBr band-systems were heavy-current uncondensed tube-discharges through continuous streams of the vapours of the tetrachloride and tetrabromide. The tetrachloride was prepared by the action of hydrochloric acid on the dioxide(18) and purified by treatment with anhydrous sodium carbonate and subsequent distillation in an all-glass apparatus (B.P. 83° C.). The tetrabromide was prepared by the prolonged action of A.R. bromine on metallic germanium(19) and purified by fractional distillation under the same rigorous conditions (M.P. 26° C., B.P. 184° C.).

The discharge carried a current of about 0·25–0·35 A. from a 2400-V. transformer whose primary was connected through a suitable rheostat to 230-V. mains (50 c./sec.); a bank of tungsten filament lamps (100 V., 40–60 W.) connected in series with the discharge tube served as an additional control and as a rough indicator of the magnitude of the secondary current.

The discharge tube, which is shown in figure 1, is of pyrex. An essential feature is the large area of contact of the cylindrical sheet electrodes with the water-cooled walls of the bulbs. For the electrodes and leads nickel* is used in preference to aluminium in order to avoid the AlCl band-system in the region of λλ2600–2700.

As the germanium compounds have to be used with as little loss as possible, their vapours cannot, of course, be continuously pumped through the discharge into tubes of soda-lime or other absorbent as in the case of cheaper material such as $SiCl_4$ or $SnCl_4$. The inflow and outflow tubes are therefore connected (through picein joints) to glass traps T_1 and T_2 provided with stopcocks A_1, B_1 and A_2, B_2.

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* The same type of tube, but without the traps T_1 and T_2 shown in figure 1, had previously been used for SiCl(6). Opportunity has now been taken to replace the impure nickel first used (which, on account of its copper content, gave rise to Cu lines and CuCl bands) by pure nickel which later became available.

One trap, say T_1, which initially contains the whole of the tetrahalide, is cooled in liquid air, and the whole apparatus as far as the closed stopcock A_1 is evacuated by an oil-pump connected to A_2. Stopcocks B_1 and A_2 are then closed and the liquid-air bath is transferred from T_1 to T_2. When the substance in T_1 has warmed up to its melting point, B_1 is partly opened so that the vapour may slowly pass through the discharge tube and freeze out in T_2. A suitable vapour pressure (as a rule, not much below the highest at which the discharge will easily pass) is maintained in the tube by adjustment of B_1 and, if necessary, occasional pumping through A_2 for a few seconds. When all the substance has passed into T_2, the liquid-air bath is returned to T_1, the pump connexion transferred to A_1, and the flow of vapour reversed; and so on throughout the time of the exposure. The discharge through either substance results in a black deposit of metallic germanium, especially in the central part *D*; and there is also a coloured deposit near the

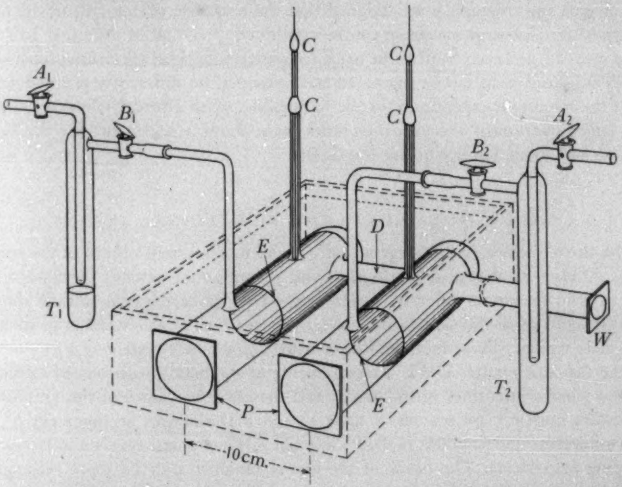

Figure 1. Water-cooled pyrex discharge tube used for continuous streams of $GeCl_4$ and $GeBr_4$ vapours. *E*, sheet nickel cylindrical electrodes. *C*, cement (picein) joints between the nickel leads and soda-glass capillary tubes and between the latter and the vertical pyrex tubes. *P*, glass plates, cemented with picein to the ground open ends of the pyrex bulbs, so that the tube may easily be dismantled for cleaning purposes. T_1 and T_2 soda-glass traps cemented with picein to the inflow and outflow pyrex tubes. The whole discharge tube, except the side tubes, is immersed in running water in an open-top paraffin-waxed wooden box shown in broken lines; the tube is supported in a cradle (not shown), also of paraffin-waxed wood, fixed down in the box. *W*, quartz window through which the column of the discharge *D* is viewed end-on, holes being made in the electrodes for this purpose; the window is cemented with picein to the extension tube which passes through a plasticine joint closing a slotted hole in the side of the box.

electrodes, which is purple in the case of the tetrachloride and light brown in that of the tetrabromide.

The desired band-systems of GeCl and GeBr were first sought in spectrograms obtained with exposures of about 30 and 15 min., respectively, in a small quartz instrument (Hilger's E 6), and the final measurements were made on spectrograms obtained with a quartz Littrow instrument (Hilger's E 1) of much larger dispersion, namely 6·40–4·25 A./mm. between λ3260 and λ2840. The diaphragm used at the slit of each spectrograph is so designed that the exposure of one-half of the total width of the discharge spectrum can be continued after that of the other half has been stopped, and each half has the usual iron-arc comparison spectrum juxtaposed. Thus any band-head can be examined and measured on differently exposed strips with the minimum expenditure of the tetrahalide. With Ilford Ordinary plates in the larger instrument the exposure times were about 1 and 2 hr. for the GeCl system and about ½ and 1 hr. for the GeBr.

§ 3. GeCl BAND-HEAD DATA AND VIBRATIONAL ANALYSIS

In the tetrachloride discharge an ultra-violet band-system occurs in the region λ3202–λ2847, as shown in figure 2(*a*), and a continuum extends from λ2660 to λ2510 with maximum intensity near λ2570. The bands degrade toward shorter wave-lengths as in the case of the SiCl, SiBr and SnCl band-systems in roughly the same region. These facts and the structure of the new system at once pointed to the diatomic emitter GeCl. Measurements of the band-heads, visual estimates of the relative intensities of the bands, and the assigned values of the vibrational quantum numbers are set out in table 1; and a Deslandres arrangement of the wave-numbers and intervals is shown in table 2. The system consists of two overlapping subsystems. The heads of the less refrangible and the more refrangible subbands are designated as (i) and (ii) respectively, in order to avoid an incorrect use of theoretically significant symbols, such as P_1 and P_2 or Q_1 and Q_2, since it is not known whether the measured heads are of P-form or of Q-form. Their wave-numbers are approximately represented by

$$\nu=\left\{\begin{matrix}33992\cdot2\\33017\cdot2\end{matrix}\right\}+(526\cdot6u'-0\cdot3u'^2)-(408\cdot4u''-1\cdot6u''^2),$$

where $u'=v'+\frac{1}{2}$ and $u''=v''+\frac{1}{2}$; the residuals, $\nu_{\text{obs.}}-\nu_{\text{calc.}}$, are included in table 1. The independent coefficients are fairly close approximations to the subsystem origins, and the electronic separation, 975 cm.$^{-1}$, represented by the difference of these coefficients, is, as would be expected, intermediate between those already quoted for the lowest states of SiCl and SnCl.

The abundance ratios of the chief isotopes⁽²⁰⁾ of Ge and Cl are

$$^{74}\text{Ge} : {}^{72}\text{Ge} : {}^{70}\text{Ge} = 100 : 73\cdot6 : 57\cdot2 \text{ and } {}^{35}\text{Cl} : {}^{37}\text{Cl} = 100 : 31\cdot4.$$

Hence in the composite GeCl system the intensities of bands of the more important isotopic emitters ^{72}Ge^{35}Cl, ^{70}Ge^{35}Cl, ^{74}Ge^{37}Cl will be about 74, 57 and 31 per cent, respectively, of those of the corresponding bands of the most abundant emitter $^{74}Ge^{35}Cl$. The values of the displacement coefficient $\rho - 1$ for these three isotopic emitters are $+0{\cdot}00445$, $+0{\cdot}00913$ and $-0{\cdot}01840$ respectively. If, then, all emitters less abundant than these be ignored, each prominent band-head of $^{74}Ge^{35}Cl$ should be accompanied by two relatively close and weaker heads due to the Ge isotope effect on the side remote from the system-origin, and by one less close and still weaker head due to the Cl isotope effect on the side towards the system-origin. No band of the system is expected, however, to be favourable for the observation of all three companion heads. Since the bands degrade in the high-ν direction the heads due to the Ge isotope effect are only likely to be detected for a strong band on the low-ν side of ν_e while a strong band on the high-ν side is

Table 1. GeCl band-heads

v', v''	Sub-band	λ_{air}	Int.	$\nu_{vac.}$	$\nu_{obs.} - \nu_{calc.}$
1, 6	(i)	3202·22	1	31219·3	−0·1
0, 4	(i)	3176·40	2*n*	473·1	−1·9
1, 5	(i)	62·80	2*n*	608·4	−0·2
0, 3	(i)	36·77	4	870·7	+0·1
0, 2	(i)	3097·99	5	32269·7	+0·3
0, 1	(i)	59·83	6	672·1	+0·7
0, 3	(ii)	43·40	2*n*	848·5	+2·9
0, 0	(i)	22·43	5	33076·4	−0·2
1, 1	(i)	11·42	2	197·3	−0·1
0, 2	(ii)	07·03	6	245·7	+1·3
1, 0	(i)	2975·09	4	602·6	0·0
0, 1	(ii)	71·25	7*d* ?	646·1	−0·3
0, 0	(ii)	36·04	8*d*	34049·5	−2·1
2, 0	(i)	29·38	4	127·0	−1·0
1, 1	(ii)	25·75	5	169·3	−3·1
1, 0	(ii)	2891·25	8*d*	577·0	−0·6
2, 0	(ii)	47·88	4*d*	35103·5	+0·5

n, nebulous, rather difficult to locate exactly; *d*, double, see text (p. 538).

Table 2. GeCl band-heads

v' ↑		v'' → 0		1		2		3		4		5		6
2	(ii)	35103·5												
		976·5												
	(i)	34127·0												
		526·5 *524·4*												
1	(ii)	34577·0	*407·7*	34169·3						—		—		—
		974·4		*972·0*										
	(i)	33602·6	*405·3*	33197·3						*		31608·4	*389·1*	31219·3
		527·5 *526·2*		*523·2* *525·2*										
0	(ii)	34049·5	*403·4*	33646·1	*400·4*	33245·7	*397·2*	32848·5		—				
		973·1		*974·0*		*976·0*		*977·8*						
	(i)	33076·4	*404·3*	32672·1	*402·4*	32269·7	*399·0*	31870·7	*397·6*	31473·1				

* Hidden by Ge line λ3124·84, ν31992·4.

more favourable for the detection of the head due to the Cl isotope effect. In the present system, bands of the former description are much the more numerous. The complex type of the bands (probably $^2\Sigma \rightarrow {}^2\Pi$, as will be seen in a later section) and the presence of incompletely resolved rotational structure of neighbouring bands in the higher-dispersion spectrograms, combine to render the detection of either isotope effect exceedingly difficult and uncertain. Additional possible heads have been observed for several of the subbands. Two of these, which are sufficiently clear of overlying band structure for measurement, have positions and intensities appropriate to heads of $^{70}Ge^{35}Cl$ and $^{74}Ge^{37}Cl$, the main system (tables 1 and 2) being attributed to $^{74}Ge^{35}Cl$. Data for these heads are as follows:

Emitter	Subband	λ^i	ν^i	$(\nu^i - \nu)_{obs.}$	$(\rho - 1)(\nu - \nu_e)$
$^{70}Ge^{35}Cl$	0 → 1 (ii)	2971·60	33642·1	− 4·0	(+0·00913) (−346) = − 3·2
$^{74}Ge^{37}Cl$	1 → 0 (ii)	2892·12	34566·6	− 10·4	(−0·01840) (+585) = − 10·8

Further possible heads, which have been measured at $\lambda 2936{\cdot}31$, $\nu 34046{\cdot}4$ for the 0 → 0 (ii) subband and $\lambda 2848{\cdot}59$, $\nu 35094{\cdot}8$ for the 2 → 0 (ii) subband, are certainly not attributable to an isotope effect, and are presumably the heads of other branches of the main $^{74}Ge^{35}Cl$ bands.

§ 4. GeBr BAND-HEAD DATA AND VIBRATIONAL ANALYSIS

The tetrabromide discharge develops a similar doublet system of bands degraded towards shorter wave-lengths in roughly the same region. This system is reproduced in figure 2(*b*) and is due, no doubt, to the diatomic emitter GeBr. The bands extend from λ3260 to λ2946, and are followed by a continuum extending from about λ2930 to about λ2850 and having a maximum intensity near λ2900. In tables 3 and 4 the band-head data are presented in the same way as those of GeCl, the low-ν and high-ν subbands being again denoted by (i) and (ii) respectively. The heads are fairly well represented by

$$\nu = \begin{Bmatrix} 33413{\cdot}4 \\ 32263{\cdot}4 \end{Bmatrix} + (383{\cdot}7u' - 0{\cdot}7u'^2) - (296{\cdot}6u'' - 0{\cdot}9u''^2),$$

in which $u = v + \frac{1}{2}$, the residuals being shown in table 3. As was to be expected, the separation of the subsystem origins is greater for GeBr than for GeCl, namely 1150 cm.$^{-1}$ as against 975.

The fuzziness of many of the heads, and the consequent difficulty of locating them exactly, may be due in part to the complexity of the bands (probably $^2\Sigma \rightarrow {}^2\Pi$ as will be seen in the following section) and in part to unresolved isotope effects. On account of the large masses and nearly equal abundances of the Br isotopes, the pattern formed by corresponding band-heads due to isotopic GeBr emitters will be rather close and complicated, even if again only the three chief Ge isotopes are considered (20). Starting with a relatively strong head (ν) due to $^{74}Ge^{81}Br$ and ending with a relatively weak one due to $^{70}Ge^{79}Br$, the pattern will consist of three pairs, in each of which the components will have equal intensities. The first pair, due to ^{74}Ge^{81}Br and ^{74}Ge^{79}Br, will have a separation of about 0·006 $(\nu-\nu_e)$ and relative intensities 100; the second, due to ^{72}Ge^{81}Br and ^{72}Ge^{79}Br, will have nearly the same separation but relative intensities 74; and the third, due to ^{70}Ge^{81}Br and ^{70}Ge^{79}Br, also nearly the same separation, but relative intensities 57. The three pairs will be very close to one another, being nearly equally spaced at about 0·0075 $(\nu-\nu_e)$. Thus, the ^{74}Ge^{79}Br and ^{72}Ge^{81}Br heads will be only about

Table 3. GeBr band-heads

v', v''	Sub-band	λ_{air}	Int.	$\nu_{\text{vac.}}$	$\nu_{\text{obs.}}-\nu_{\text{calc.}}$
1, 7	(i)	3259·69	1*n*	30669·0	+5·5
0, 5	(i)	40·75	2*n*	848·2	−2·8
1, 6	(i)	30·48	2*n*	946·3	−1·2
0, 4	(i)	10·73	3	31136·6	−2·0
1, 5	(i)	00·67	3*n*	234·5	+1·2
0, 3	(i)	3181·04	5*n*	427·2	−0·8
1, 4	(i)	71·65	3*n*	520·2	−0·7
0, 2	(i)	51·65	7	720·3	+1·1
0, 1	(i)	22·81	7	32013·2	+1·0
1, 2	(i)	14·16	5	102·1	+0·6
0, 4	(ii)	3096·44	4*d* ?	285·8	−2·8
0, 0	(i)	94·33	5	307·8	+0·8
1, 1	(i)	86·02	7	394·8	+0·3
0, 3	(ii)	68·83	8	576·3	−1·7
1, 0	(i)	58·48	6*n*	686·5	−2·8
0, 2	(ii)	41·34	10	870·7	+1·5
0, 1	(ii)	14·68	10	33161·4	−0·8
1, 2	(ii)	06·36	8	253·2	+1·7
0, 0	(ii)	2987·99	8	457·6	+0·6
1, 1	(ii)	80·22	10	544·8	+0·3
1, 0	(ii)	54·24	12	839·8	+0·5
2, 1	(ii)	46·76	5	925·7	+0·3

n, nebulous, rather difficult to locate exactly; *d*, double, see text (p. 540).

Table 4. GeBr band-heads

v' ↑		v'' → 0		1		2		3		4		5		6		7
2	(ii)			33925·7												
	(i)			—												
				380·9												
				—												
1	(ii)	33839·8	*295·0*	33544·8	*291·6*	33253·2				—		†		‡		§
		1153·3		*1150·0*		*1151·1*										
	(i)	32686·5	*291·7*	32394·8	*292·7*	32102·1				31520·2	*285·7*	31234·5	*288·2*	30946·3	*277·3*	30669·0
		382·2		*383·4*		*382·5*				—		—				
		378·7		*381·6*		*381·8*				*383·6*		*386·3*				
0	(ii)	33457·6	*296·2*	33161·4	*290·7*	32870·7	*294·4*	32576·3	*290·5*	32285·8		*				
		1149·8		*1148·2*		*1150·4*		*1149·1*		*1149·2*						
	(i)	32307·8	*294·6*	32013·2	*292·9*	31720·3	*293·1*	31427·2	*290·6*	31136·6	*288·4*	30848·2				

* Hidden by Ge line λ3124·84, ν31992·4.
‡ Hidden by structure of 0→1 subband (i).
† Hidden by structure of 0→0 subband (i).
§ Hidden by structure of 0→2 subband (i).

$0{\cdot}0015\ (\nu-\nu_e)$ apart and will probably be observed as a blend (*a*) with relative intensity approaching $100+74$; and similarly the ^{72}Ge^{79}Br and ^{70}Ge^{81}Br heads will probably be observed as a blend (*b*) with relative intensity approaching $74+57$. It seems reasonable to ascribe each of the heads in tables 3 and 4 to the stronger blend (*a*), and then examine each strong and favourably placed subband either for the ^{74}Ge^{81}Br head at about $-0{\cdot}0065\ (\nu-\nu_e)$ or for the weaker blend (*b*) and the ^{70}Ge^{79}Br head at about $+0{\cdot}007\ (\nu-\nu_e)$ and $+0{\cdot}014\ (\nu-\nu_e)$ respectively. No subband is expected to be favourable for the observation of all of these, and, moreover, the calculated displacements are rather small for all the strong subbands. While this interpretation is probably correct, no bands attributable to an isotope effect have been measured with certainty. In the $0 \rightarrow 4$ (ii) subband a rather doubtful second head is observed which may be blend (*b*); the data are: $\lambda^i = 3097{\cdot}21$, $\nu^i = 32277{\cdot}8$, $(\nu^i-\nu)_{\text{obs.}} = 8{\cdot}0$, $(\nu^i-\nu)_{\text{calc.}} = 7{\cdot}9$ cm.$^{-1}$

§ 5. DISCUSSION OF RESULTS

Analogy with SiCl and SnCl suggests that the electronic intervals of 975 and 1150 cm.$^{-1}$ established by the foregoing analyses occur entirely in the lower states of GeCl and GeBr, and that these are $^2\Pi$ ground states.

The observed electronic intervals $\delta\nu_e$ and vibrational coefficients ω_e'' and $x_e''\omega_e''$ for the lowest states of this subgroup of diatomic halides are collected in table 5. In each case, as the atomic number and mass of either the group-IV (*b*) atom or the halogen increase, the expected trend is observed: namely, an increase in $\delta\nu_e$ (apart from the possibly exceptional cases of the Pb halides already discussed on p. 533) and decreases in ω_e'' and $x_e''\omega_e''$. The regularities shown by these latter suggest, as a further step, a comparison of the rough estimates of the dissociation energies D obtained by extrapolation of the vibrational energies for these states by means of the well-known expression

$$D = (\omega_e - x_e\omega_e)^2/(4x_e\omega_e \times 8106)\ \text{e.V.}$$

The values of D are also shown in table 5. Although they are subject to large errors on account of inaccuracies in the small coefficients $x_e''\omega_e''$, it is evident that their trend is the same as that of ω_e'' and $x_e''\omega_e''$.

The foregoing assumption that the observed GeCl and GeBr separations occur wholly in the lower states implies, of course, that the upper states have single electronic levels, as in the case of the $\lambda 2924$ system ($\text{B}\,^2\Sigma(?) \rightarrow \text{X}\,^2\Pi$) of SiCl and the $\lambda 2973$ system ($^2\Sigma \rightarrow {}^2\Pi$) of SnCl.* If the upper states in these four cases are truly comparable we should expect to find that the electronic energy (as determined by the greater of the two subsystem origins) in GeCl is greater than that in GeBr and intermediate between the electronic energies in SiCl and SnCl. This is, in fact, observed to be the case, as will be seen in table 6, where these electronic energies

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* The present suggestion that these are comparable systems requires an amendment to figure 2 in the paper on SiCl(6). The broken lines connecting D to $^2\Sigma$ and C to $^2\Delta$ should be replaced by one connecting B to $^2\Sigma$.

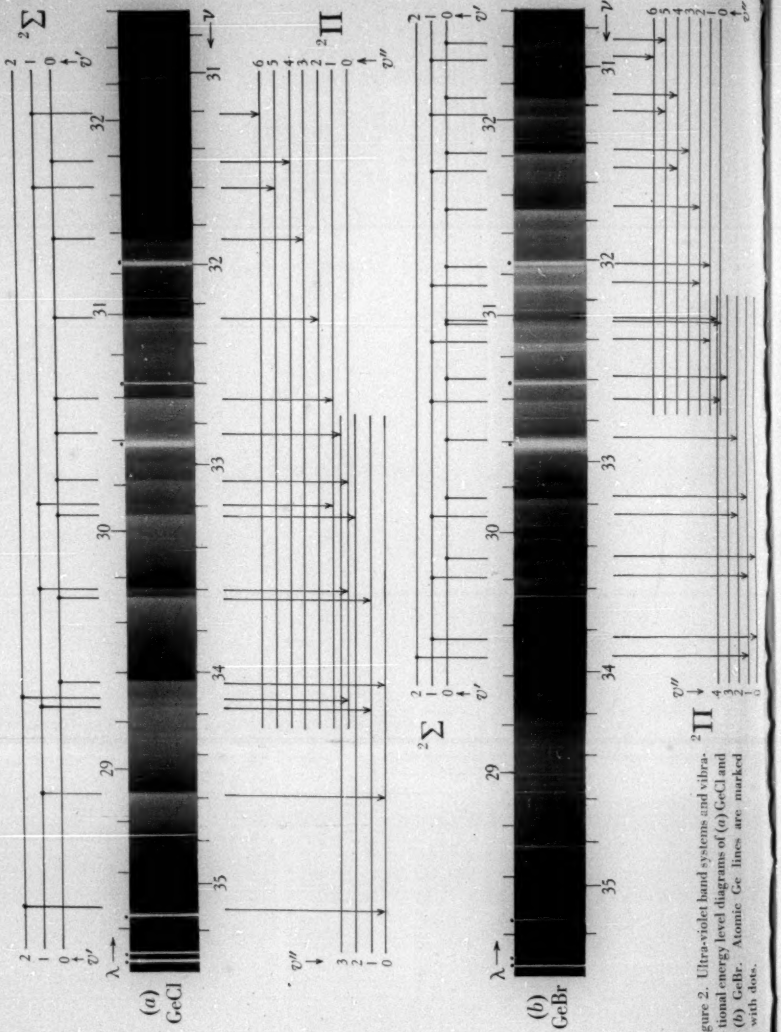

Figure 2. Ultra-violet band systems and vibrational energy level diagrams of (*a*) GeCl and (*b*) GeBr. Atomic Ge lines are marked with dots.

To face page 541

are set out with the corresponding data from the λ2880 system ($B\,^2\Sigma \rightarrow X\,^2\Pi$) of SiF and from the only recorded systems of PbF, PbCl, PbBr, SiBr and CCl. Table 6 also shows the total energies of the $v = 0$ levels (as determined by the wave-number of the more refrangible component of the $0 \rightarrow 0$ band in each system) and the vibrational coefficients ω_e' and $x_e'\omega_e'$. Here again, with increasing atomic number and mass of either atom, the expected trend is observed in each case, namely a slight decrease in ν_e, a corresponding red-shift of the $0 \rightarrow 0$ band, and decreases in ω_e' and $x_e'\omega_e'$, except for $x_e'\omega_e'$ of GeCl where the estimate is rather unreliable as the observed bands with $v' = 1$ and 2 are too few.

Table 5. Data for lower ($^2\Pi$) states

	Electronic separation $\delta\nu_e$ (cm.$^{-1}$)			ω_e'' (cm.$^{-1}$)			$x_e''\omega_e''$ (cm.$^{-1}$)			Dissociation energy, D'' (e.V.)		
	F	Cl	Br	F	Cl	Br	F	Cl	Br	F	Cl	Br
C		136			(843·6)‡							
Si	161	208	418*	856·7	535·4	425·4*	4·7	2·20	1·5*	4·8	4·0	3·7
Ge		975	1150		408·4	296·6		1·6	0·9		3·2	3·0
Sn		2360	2467†		353·5	247·7†		1·2	0·62†		3·2	3·0†
Pb	0?	0?	0?	506·9	304·2	207·5	2·29	0·89	0·50	3·4	3·2	2·6

Table 6. Data for upper ($^2\Sigma$) states

	Electronic energy (system-origin) ν_e (cm.$^{-1}$)			Energy of $v = 0$ level above that of lower state (cm.$^{-1}$)			ω_e' (cm.$^{-1}$)			$x_e'\omega_e'$ (cm.$^{-1}$)		
	F	Cl	Br	F	Cl	Br	F	Cl	Br	F	Cl	Br
C					35975			(863)§				
Si	34639·4	34102·7	33571·0*	34716·6	34185·3	33645·6*	1011·2	(698·7)§	573·6*	4·8		3·1*
Ge		33992·2	33443·4		34049·5	33457·6		526·6	383·7		0·3	0·7
Sn		33582·6			33622·6	33094·5†		432·5			1·2	
Pb	22565·2	21866·9	20884·3	22510·4	21829·8	20856·8	397·8	228·6	152·5	1·77	0·76	0·4

* SiBr data taken from a forthcoming paper (15) in preference to those given in the preliminary note (14).

† SnBr data taken from a forthcoming paper (15).

‡ Value of $\omega_{\frac{1}{2}}''$ inserted for CCl (17) as ω_e'' and $x_e''\omega_e''$ are not known for lack of bands with $v \geqq 2$.

§ Value of $\omega_{\frac{1}{2}}'$ inserted for CCl (17) and SiCl (6) as ω_e' and $x_e'\omega_e'$ are not known for lack of bands with $v \geqq 2$.

In conclusion, then, it would appear that the band systems of GeCl and GeBr, like those cited for SiF, CCl, SiCl and SnCl, are due to transitions $^2\Sigma \rightarrow {}^2\Pi$, the lower states being the ground states. In view of this result, the anomaly mentioned in the introduction, that SiBr appears to have a single level as its lower state, becomes even more striking. New investigations of the spectrum of SiBr and that of SnBr (for which data have hitherto been lacking) are described in a forthcoming paper (15), some data from which are included in tables 5 and 6 for the sake of completeness. In each case it appears that the ground state is a doublet (probably $^2\Pi$) with electronic separations of 424 and 2710 cm.$^{-1}$ respectively. Thus, as the preliminary note (14) indicated, the apparent anomaly in the case of SiBr is removed.

§ 6. ACKNOWLEDGMENTS

The authors have pleasure in recording their indebtedness to Prof. Sir Gilbert Morgan and Dr G. R. Davies for the gift of germanium, germanium dioxide and other germaniferous material from which the tetrachloride and tetrabromide were prepared. They also express their thanks to the Government Grant Committee of the Royal Society for grants for apparatus; to the Fereday Electors of St John's College, Oxford, for the opportunity afforded to one of them (W. J.) of taking part in this work; and to the Governors of Collyer's School, Horsham, and the Education Committee of the West Sussex County Council for personal grants to another (L. A. B.).

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THE ULTRA-VIOLET BAND-SYSTEM OF GERMANIUM MONOXIDE

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Received 21 *April* 1937. *Read in title* 11 *June* 1937

ABSTRACT. The GeO band-system, recently investigated by Shaw between λ2989 and λ2441 in the flame surrounding an arc charged with GeO_2, has been measured over the larger range λ3319–λ2441 in an uncondensed discharge through a mixture of $GeCl_4$ vapour and oxygen flowing continuously through the discharge tube. The number of bands measured is increased from 18 to 32, and the highest observed value of v'' from 5 to 10. The band-heads of the extended system are approximately represented by

$$\nu = 37762{\cdot}4 + (651{\cdot}3u' - 4{\cdot}24u'^2) - (985{\cdot}7u'' - 4{\cdot}30u''^2),$$

where $u = v + \frac{1}{2}$. This system being attributed to ^{74}GeO, a few other observed heads may be due to ^{72}GeO and ^{70}GeO. Rotational analysis being impossible, there is no further evidence for or against the transition $^1\Pi \rightleftarrows {}^1\Sigma$ suggested by Shaw. The data are compared with those for band-systems of other monoxides and monosulphides of group-IV*b* elements, and the observed decreases of ν_e, ω_e and $x_e\omega_e$ with increasing atomic number or mass of either atom are shown graphically.

§ 1. INTRODUCTION

RECENTLY, R. W. Shaw⁽¹⁾ has analysed the vibrational structure of a system of GeO bands, degraded towards the red and extending from λ2989·3 to λ2441·0. The source used was the flame surrounding an 8–10 A. arc in air between graphite rods charged with germanium dioxide. In spectrograms taken with a quartz Littrow instrument (Hilger's E 1, dispersion about 4·7 to 2·5 A./mm. in this region) twenty-one bands were observed, and the *R* heads of eighteen of them were measured and closely represented by the formula

$$\nu = 37763{\cdot}7 + (649{\cdot}4u' - 3{\cdot}81u'^2) - (985{\cdot}0u'' - 4{\cdot}36u''^2),$$

where u' and u'' are written for $v' + \frac{1}{2}$ and $v'' + \frac{1}{2}$; the heads of the other three observed bands were obscured by atomic lines. Estimates of the relative intensities of the bands were not very reliable and any attempt at rotational analysis was inadvisable, on account of overlapping of bands: this is readily understandable in view of the high-temperature distribution of line intensities in each branch of the bands in the source employed.

In order to obtain greater contrast between a band-head and the overlying structure of neighbouring bands a source giving a lower temperature distribution would appear to be necessary. One such source, which had already been used for the ultra-violet systems of the analogous emitters SiO(2) and SnO,* was clearly applicable to the GeO system, and was, in fact, being so applied when Shaw's recent paper appeared. An uncondensed discharge is passed through a mixture of oxygen and the chloride vapour ($SiCl_4$, $SnCl_4$ or $GeCl_4$) pumped continuously through the discharge tube. With comparatively little oxygen in the mixture the bands of the monoxide are accompanied by those of the monochloride, but with sufficient oxygen the latter may be entirely quenched, so that the monoxide bands are developed with little but a few strong atomic lines to interfere with good measurement. As this is a very convenient method, which, judging from published observations, has been little used, it would seem desirable to redirect attention to it, especially as its employment is now greatly facilitated by the substitution of a suitable transformer for the induction coil previously used in the cases of SiO and SnO.

Apart from the question of intensity distribution, this discharge-tube method is more economical in material than the arc in air; this is an important advantage in the case of GeO. In this work the band-system has been considerably extended by the measurement of band-heads not previously measured and by the recognition of some heads due to the germanium isotope effect. It seemed, therefore, that there would be no advantage in making observations either with the arc in air as used by Shaw, or with the uncondensed discharge through a flame as used by Connelly(5) for the SnO bands. It might be added that, even had they been desirable, neither of these sources could have been employed with the limited supply of germanium available.

§ 2. EXPERIMENTAL

The germanium tetrachloride used was a part of that already prepared for the investigation of the GeCl band-system(7). As in that work, the discharge carried a current of about 0·3 A. from a 2400-V. transformer connected to the 230-V. supply of A.C. at 50 c./sec. The same water-cooled pyrex discharge tube with large cylindrical electrodes of nickel sheet was used, but for the present purpose the inlet tube leading to one of the electrode bulbs has two branches, one connected to a bulb containing the tetrachloride, and the other to an oxygen cylinder. The exit tube leading from the other electrode bulb is connected, as in the previous work, through a trap to an oil-pump.

With both bulb and trap immersed in liquid air, the apparatus is evacuated and flushed through with oxygen at low pressure, and the discharge is started. The tetrachloride bulb is then immersed in a bath of alcohol cooled with solid carbon dioxide to about −30° C. By careful adjustment of the stopcocks in the two inlet branches it is easy to admit the required amounts of the tetrachloride and oxygen, the appearance of the glow on the electrode near the inflow tube affording a reliable guide to their correct proportioning. The glow on each electrode is blue when oxygen alone is admitted, and pink with tetrachloride alone. With a mixture of the two in certain proportions the glow on the first (inflow) electrode is blue and that on the second (outflow) electrode is pink, and the spectrum of the column of the discharge shows the GeO system almost entirely free from the GeCl system. This is the mixture which it is sought to maintain throughout the spectrographic exposure. With a slight reduction in the flow of oxygen or a slight increase in that of the tetrachloride the glow on the first electrode changes from blue first to a greyish or neutral tint and then to pink, and the GeCl band-system appears in the spectrum of the column; care is taken just to avoid this condition throughout the exposure. Free chlorine and any tetrachloride which has escaped decomposition in its passage through the discharge are condensed in the trap, which remains immersed in liquid air. A white deposit of the dioxide is formed on the walls of the discharge tube.

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* Unpublished work, put aside for the preparation of this Society's *Report*(3). The SnO bands were afterwards observed and measured by Mahanti, using an arc in air(4), and by Connelly, using an uncondensed discharge through a flame(5). The unpublished measurements and analysis were in close agreement with Connelly's. The present method had previously been used also in observations of the BO bands and the other boron oxide (B_2O_3?) bands(6).

A quartz spectrograph (a forerunner of Hilger's E 2) of medium dispersion (22 to 8 A./mm. from λ 3320 to λ 2441) was used in the first stages. A five minutes' exposure of an Ordinary plate sufficed to record the whole system between these wave-lengths, and further exposures up to an hour were also made in an unfruitful search for a weaker system. The greater part of the system, excluding only a few of Shaw's more refrangible bands, was afterwards photographed on an Ordinary plate exposed for 20 and 50 min. in a large quartz Littrow instrument (dispersion 5·3 to 2·2 A./mm. in the range λ3320 to λ2530). Only 2–3 c.c. of the liquid tetrachloride was used for these spectrograms. In view of an earlier observation(8) that hot germanium monoxide vapour tends to form a glaze on quartz windows which prevents the taking of satisfactory absorption spectrograms, it may be mentioned here that no such action has been detected in the course of the present observations.

§ 3. BAND-HEAD MEASUREMENTS AND VIBRATIONAL ANALYSIS

In the smaller spectrograms, one of which is reproduced in figure 1 *a*, the GeO bands appear with single (R) heads; and in spite of the fact that the conditions in the discharge had not secured the complete elimination of the strongest GeCl bands(7), the GeO heads were measurable over the whole range λ 3320–λ2441. No undue difficulty or uncertainty arose except where the system merges into a continuum which extends from about λ2630 to about λ2380 and has its maximum intensity near λ2560. It was evident from the first measurements that all the bands belong to a single system, which thus extends beyond the GeCl system in both directions, and not only in the short-wave direction as had appeared from the arc observations(1). In the larger spectrogram, a part of which is reproduced in figure 1 *b*, some of the bands appear to have two or even three heads; in such cases all the more certain heads were measured, but only the most refrangible (R) head of each band is considered at present. In table 1 the data from this spectrogram are given to six significant figures and those from the smaller spectrograms to five. The incom-

Table 1. Deslandres arrangement of data for band-heads of ^{74}GeO. Wave-lengths in air are printed in Italics, rough estimates of intensity in Italics in parentheses, wave-numbers *in vacuo* in large Roman type and differences between wave-numbers in small Roman type.

$v' \uparrow$ $v'' \rightarrow$	0		1		2		3		4		5		6		7		8		9		10
7			*2441·9 (2)* 40939																		
			593																		
6			*2477·8 (3)* 40346*																		
			595																		
5	*2454·8 (4)* 40724	973	*2514·88 (4)* 39751·4																		
	611																				
4	*2492·2 (5)* 40113		‡		*2619·5 (4)* 38164*																
	616				614																
3	*2531·10 (5)* 39496·6		‡		*2662·33 (4)* 37549·9*	962	*2732·3 (4)* 36588*										*3131·6 (3)* 31923*	904	*3222·9 (2)* 31019*	902	*3319·4 (2)* 30117*
	625·4				625		624										626		630		
2	*2571·83 (5)* 38871·2	977·4	*2639·17 (2)* 37893·8	969	*2707·4 (3)* 36925*	961	*2779·71 (6)* 35964·4	953·5	*2855·42 (4)* 35010·9						*3103·1 (3)* 32217*	920	*3194·3 (3)* 31297*	908	*3289·7 (2)* 30389*		
	633·4		632·9						634						640						
1	*2614·43 (5)* 38237·8	976·9	*2682·98 (8)* 37260·9		†		†		*2908·1 (8)* 34377	941	*2989·89 (5)* 33436·3	932	*3075·7 (3)* 32504*	927	*3165·9 (2)* 31577*						
	646·8		642·0						637		645·6										
0	*2659·42 (3)* 37591·0	972·1	*2730·02 (8)* 36618·9	968·2	*2804·17 (10)* 35650·7	959·7	*2881·75 (10)* 34691·0	951·7	*2963·04 (7)* 33739·3	948·6	*3048·76 (5)* 32790·7*										

* Band-heads not hitherto recorded.

† The 1 → 3 and 1 → 2 band-heads are obscured by the Ge lines λ2829·09, ν35336·7 and λ2754·59, ν36292·3 respectively.

‡ The 3 → 1 and 4 → 1 band-heads are obscured by the strong continuum; they are near λ2595·3, ν38519 and λ2554·6, ν39133 respectively, and clear of the Ge lines λ2592·55 and λ2556·32.

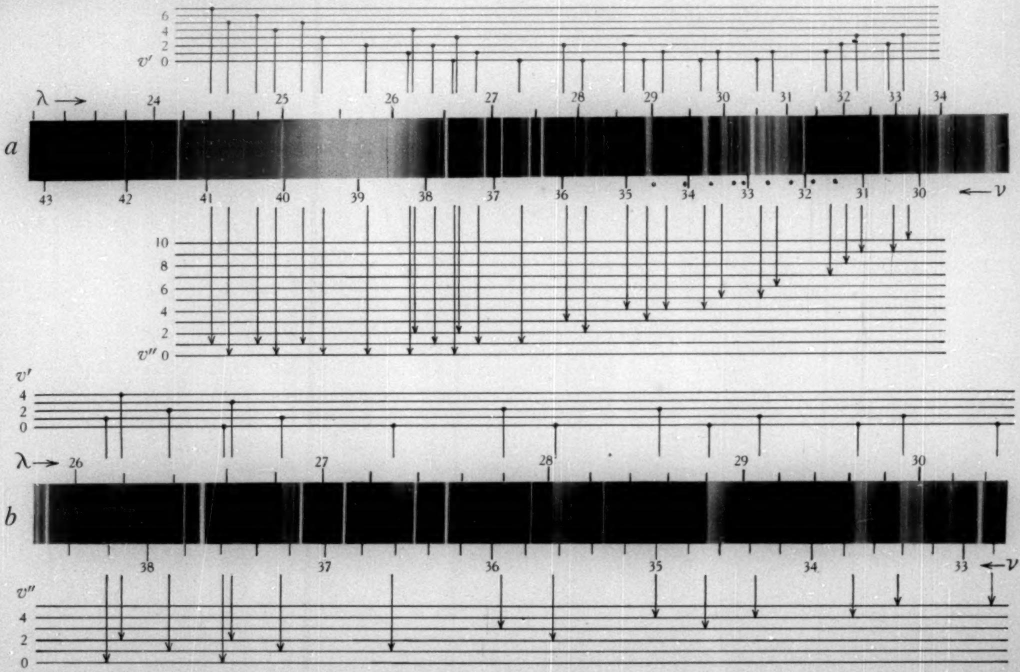

Figure 1. GeO bands in an uncondensed discharge through mixture of O_2 and $GeCl_4$: (*a*) the whole system in medium dispersion (Hilger's E2); (*b*) part of the system in higher dispersion (large Littrow spectrograph). All the strong atomic lines are Ge. The dots mark heads of unquenched GeCl bands, degraded in opposite direction to GeO bands. The black vertical lines in strip (*a*) are due to small holes in the film of the photographic plate and the use of a cylindrical lens in the enlarger.

pleteness of the former data is due to two facts: (i) the length of plate used (12 in.) is not enough to cover the whole system in a single setting, and (ii) the OH bands at λ3064 and λ2811 appeared in the larger spectrogram as a result of an accidental leakage of a trace of water-vapour into the tube. It was decided to rely on the smaller spectrograms for some of the bands rather than use more germanium tetrachloride for another exposure in the larger instrument.

To avoid another table of data, the wave-lengths and rough visual estimates of intensities are inserted above the wave-numbers in the Deslandres scheme (Table I), Shaw's data are omitted, and the band-heads now measured for the first time are denoted by an asterisk. These additions to the former observations pertain chiefly to the higher values of the vibrational quantum number of the lower state ($v''=5$ to 10). The more extensive data are not satisfactorily represented by Shaw's formula, either in its original form as already quoted or with a slight modification of the independent coefficient (ν_e approximately) to allow for the fact that, on the whole, the present wave-numbers are slightly lower than Shaw's. A better representation, especially for the higher values of v' and v'', is afforded by

$$\nu = 37762\cdot 4 + (651\cdot 3u' - 4\cdot 24u'^2) - (985\cdot 7u'' - 4\cdot 30u''^2),$$

where, as before, u is written for $v+\frac{1}{2}$. Even this formula leaves residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) considerably larger than Shaw's, which are surprisingly small. It is the extent of the present data rather than any unusual accuracy that appears to the writers to be the useful feature. An unexplained difficulty arises in the identification of the head of the $0 \rightarrow 0$ band, which, although not expected from the wide-open Condon curve of intensity distribution to be a prominent band of the system, is undoubtedly present and is easily seen near the $3 \rightarrow 2$ band-head in the prints from which figure 1 has been made. Shaw's wave-number, 37596·1, for this head agrees closely with that calculated from any formula, such as his own or the present one, in which the independent coefficient is so chosen that the smallest residuals occur for the best measured heads. The present spectrograms, however, show nothing that can be interpreted as a head in this position, but give either 37591·0 or 37600·8 as the apparent position of the head; the former, which seems the more probable, is about 4 cm.$^{-1}$ less, and the latter about 6 cm.$^{-1}$ greater, than the calculated wave-number.

We have now to see whether any of the additional band-heads previously mentioned can be attributed to the Ge isotope effect. The relative abundances of the five known isotopes ^{74}Ge, ^{72}Ge, ^{70}Ge, ^{73}Ge, ^{76}Ge are 37·1, 27·3, 21·2, 7·9, 6·5 respectively$^{(9)}$. In the GeO spectrum, therefore, the bands of ^{72}GeO and ^{70}GeO will have about 0·74 and 0·57, respectively, of the intensity of the corresponding bands of the most abundant molecule ^{74}GeO, whilst those of ^{73}GeO and ^{76}GeO, having only about 0·21 and 0·18 of that intensity, may be ignored in the first instance. The vibrational displacements of bands of the lighter molecules ^{72}GeO and ^{70}GeO from those of the heavier molecule ^{74}GeO are in a direction away from the system-origin ν_e throughout the system, and are given by

$$\nu^i - \nu = (\rho - 1)(\nu - \nu_e) \text{ approximately,}$$

where the coefficient $\rho-1$ takes the values $+0{\cdot}00247$ and $+0{\cdot}00507$ respectively, ^{16}O alone being considered with each Ge isotope.

It is reasonable to assign the system in table 1 to ^{74}GeO. As the bands are degraded towards the red, the most favourable bands for the detection of ^{72}GeO and ^{70}GeO heads would normally be those on the high-ν side of the system-origin, 37762·4. In the discharge, however, a continuum extending over a considerable part of this region reduces the chance of detecting these heads, and the only promising bands seem to be the strongest and least confused bands on the low-ν side of ν_e, which are quite clear of the continuum. Additional heads have, in fact, been measured for several such bands and for one band on the high-ν side. The data in table 2, though very fragmentary and of no great accuracy, suggest that some features of the Ge isotope effect have been recognised.

Table 2. Observed band-heads of ^{72}GeO and ^{70}GeO

v', v''	^{72}GeO				^{70}GeO			
	λ^i	ν^i	$\nu^i-\nu$ obs.	calc.	λ^i	ν^i	$\nu^i-\nu$ obs.	calc.
1, 5	2990·64	33427·9	−8·4	−10·6				
0, 4	2963·87	33729·8	−9·5	−9·9	2964·67	33720·7	−18·6	−20·4
0, 2	2804·60	35645·2	−5·5	−5·2	2805·02	35639·9	−10·8	−10·7
0, 1				−2·8	2730·40	36613·9	−5·0	−5·8
1, 1				−1·2	2683·22	37257·6	−3·3	−2·5
2, 0				+2·7	2571·52	38875·9	+4·7	+5·6

§ 4. DISCUSSION

Shaw states that the available evidence favours $^1\Pi \rightarrow {}^1\Sigma$ rather than $^1\Sigma \rightarrow {}^1\Sigma$ as the electronic transition producing the system, the lower state being undoubtedly the ground state since bands of this system occur in absorption(8). In the larger spectrogram of the discharge some of the bands are fairly well resolved over short and isolated ranges remote from band-heads, but the confusion at the heads prevents any attempt at analysis of rotational structure. All that can be stated at present is that the structure appears to be too complex for $^1\Sigma \rightarrow {}^1\Sigma$, and that Shaw's interpretation of the system as the analogue of the CO Fourth Positive system and the corresponding systems, $\mathrm{A}^1\Pi \rightarrow \mathrm{X}^1\Sigma$, of CS and SiO seems the more probable, although the complexity must be due in part to the Ge isotope effect.

Now in the case of what appear to be analogous band-systems of some monohalides of group-IV*b* elements(7), the observed changes of the molecular constants with increase of atomic number and mass of either atom are, as was to be expected, an increase of the electronic separation $\delta\nu_e$ in the $^2\Pi$ ground state, a decrease or "red-shift" of the system-origin ν_e, and a decrease of each of the vibrational coefficients ω_e and $x_e\omega_e$ in both the upper and the lower electronic states. Similar decreases are expected in case of corresponding band-systems of the monoxides and monosulphides of group-IV*b* elements.

In applying the test, we take the data of this GeO system and the above systems of CO(10), CS(11) and SiO(12). For SiS no observations have been recorded, and no system of any of the other molecules has been interpreted as $^1\Pi \rightarrow {}^1\Sigma$. For GeS(3, 8) and SnS(13) two and three systems, respectively, have been observed in absorption but the transitions have not been determined; the strong systems, A ← X of GeS and B ← X of SnS, are taken. For SnO the strong system observed in emission and absorption is tentatively ascribed to a transition $A^1\Sigma \rightleftarrows X^1\Sigma$, and the remaining bands have not been satisfactorily interpreted(5). PbO has five emission and absorption systems(14), the strongest of which ($B \rightleftarrows X^1\Sigma$) is taken; for two of the other systems (D ⇄ X and A ⇄ X) rotational analysis has established the transition $^1\Sigma \rightleftarrows {}^1\Sigma$. The PbS absorption bands form five systems(15) the transitions for which are undetermined; either of the two less refrangible systems (A ← X and B ← X) serves the present purpose, and the second is taken as for PbO.

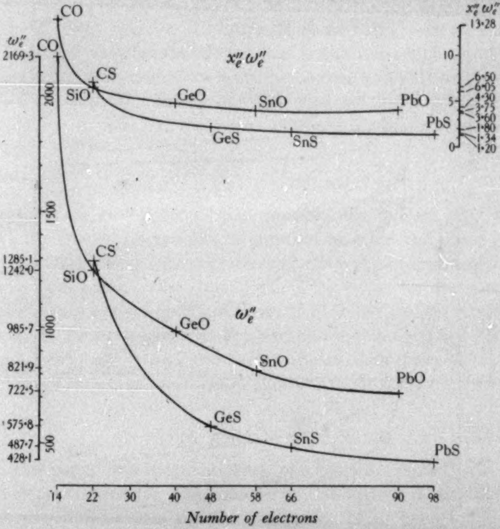

Figure 2. Variations of vibrational coefficients in the ground states of monoxides and monosulphides of group-IV*b* elements.

For the ground states, which are probably all $^1\Sigma$, the results of the test are shown in figure 2, where ω_e'' and $x_e''\omega_e''$ are plotted against the number of electrons in the molecule. The points lie on uninflected curves for the oxides and for the sulphides and the variations are as stated above, with the single exception that $x_e''\omega_e''$ is very slightly smaller, instead of larger, for SnO than for PbO; the difference is so small (0·15 cm.$^{-1}$) that it might well be changed in sign as well as in magnitude as a result of remeasurement of one of the systems concerned. CS and SiO, the only iso-electronic pair of molecules, have very close values of ω_e'' and of $x_e''\omega_e''$, CS having slightly the higher value of each (even on the small scale of reproduction of figure 2, the intersection of the curves can easily be seen, especially for ω_e''). The curves are of the same general form as those given by Shaw⁽¹⁾ for the spectroscopic estimates of the dissociation energies (D_e'') of these ground states. In contrast to the curves

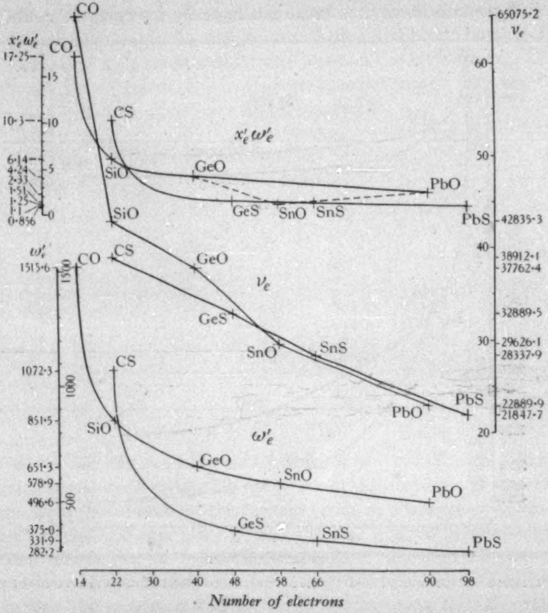

Figure 3. Variations of energies of excitation (ν_e) and vibrational coefficients of the upper states for some band-systems of monoxides and monosulphides of group-IV*b* elements.

for ω_e'' and $x_e''\omega_e''$, however, Shaw's curves for D_e'' show a higher value for PbS than for PbO.

In figure 3, the corresponding curves for the excited states show similar variations in ω_e' and $x_e'\omega_e'$, but with a bigger difference of values for CS and SiO and a much bigger discrepancy in the value of $x_e'\omega_e'$ for SnO. The diagram also includes the graphs of the system-origins, i.e. the energies of excitation of upper electronic states; although no uninflected curves can be drawn through the points the variation is as described above for the monohalides.

To sum up, the observed changes in all the constants (except $x_e'\omega_e'$ of SnO) are of the kind to be expected on the assumption that the band-systems considered correspond to the CO Fourth Positive, $A^1\Pi \rightarrow X^1\Sigma$, but they are not a sufficient proof that such is the case. Although the general decrease of ω_e with increase of molecular mass or electron number is already well known for this group and others, attention has not hitherto been directed, so far as the writers are aware, to the smoothness of the decreases of ω_e and $x_e\omega_e$ shown in figures 2 and 3. From these diagrams it seems safe to predict that SiS (30 electrons) will have a band-system, probably $^1\Pi \rightleftarrows {}^1\Sigma$, with bands degraded towards the red and roughly represented by

$$\nu = 37000 + (550u' - 3u'^2) - (850u'' - 3u''^2),$$

the $0 \rightarrow 0$ band being near $\lambda 2713$. Preparations are being made for a search for this system. Finally it may be mentioned that if the reduced mass (μ)[*] is used as abscissa instead of the number of electrons, smooth and almost uninflected curves are obtained for all the five constants for the monosulphides, giving about the same predicted values for SiS, but the curves obtained for the monoxides are of a less simple form.

§ 5. ACKNOWLEDGMENTS

The authors are glad to record their indebtedness to Prof. Sir Gilbert Morgan and Dr G. R. Davies for the gift of germanium oxide and other germaniferous material from which the germanium tetrachloride was prepared, and to the Government Grant Committee of the Royal Society for grants for apparatus. They also record their thanks to the Fereday Electors of St John's College, Oxford, for giving one of them (W. J.) the opportunity of taking part in this work, and to the Governors of Collyer's School, Horsham, and the Education Committee of the West Sussex County Council for personal grants to another (L. A. B.).

NOTE ADDED 11 JUNE 1937

Since this paper was communicated, one by Sen Gupta(16) has appeared recording new and extensive observations of this system in the carbon arc with potassium germanifluoride in the lower (+) pole, the arc being found to be steadier with this substance than with the dioxide. Exposures of an hour and a half were made in a quartz Littrow spectrograph (Hilger's E 1) similar to that used by Shaw, of whose recent paper Sen Gupta was evidently unaware since he refers only to the earlier abstract(1). To add a table here for the comparison of the three sets of data now available would involve needless expense, but the following remarks may usefully be made.

Sen Gupta has measured forty-six band-heads extending from λ 3292 to λ 2342 and finds that they are approximately represented by

$$\nu = 37775{\cdot}65 + (651{\cdot}9u' - 4{\cdot}2u'^2) - (981{\cdot}2u'' + 3{\cdot}6u''^2).$$

The present observations include twenty-six of these heads, and for ten of the

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[*] Values of $10^{24}\mu$ (gr.):

CO	11·31	SiO	16·80	GeO	21·62	SnO	23·25	PbO	24·49
CS	14·40	SiS	24·67	GeS	36·67	SnS	41·62	PbS	45·78

twenty-six (including all the strong heads from the 0 → 5 to the 5 → 1) the two sets of measures agree fairly well, the biggest differences ($\nu_{S.G.} - \nu_{\text{authors}}$) being −1·3 and +1·1 cm.$^{-1}$ for the 0 → 1 and 3 → 0 heads. In view of our remark on the 0 → 0 band (*vide supra*, p. 547), it may be noted here that Sen Gupta's result, 37591·6 cm.$^{-1}$, supports our figure rather than Shaw's. For the remaining sixteen heads common to the two investigations the agreement is less satisfactory, particularly large differences ($\nu_{S.G.} - \nu_{\text{authors}}$) being found for the 2 → 9, 2 → 4, 3 → 3, 2 → 2, 3 → 2 and 4 → 2 heads, namely −23, +6·6, +11·9, +7, +9·1 and +10·2 cm.$^{-1}$ respectively. It seems probable that the identification of these six heads is erroneous in one investigation or the other. Sen Gupta measures the four heads marked † and ‡ in our table 1; and at the high-ν end of the system ($\nu > 39300$ cm.$^{-1}$), where a continuum prevents observation of band-heads in our discharge spectrum, he records eight additional weak heads with $v' = 6$, 8, 9, 10. At the low-ν end ($\nu < 37300$) eight heads (mostly weak) are given only by Sen Gupta, and six (apparently rather stronger) occur only in our table.

Whereas Sen Gupta's wave-lengths, as is to be expected with his dispersion, are given to six significant figures, his wave-numbers are stated to seven, thus implying a precision in the latter which they do not in fact possess. This practice is, of course, to be deprecated.

Sen Gupta observes ^{72}GeO heads of the 2 → 0, 3 → 0 and 4 → 0 bands and ^{70}GeO heads of the 1 → 0, 2 → 0 and 3 → 0 bands. As we have pointed out on p. 548, these bands on the high-ν side of the system-origin are the most favourable for the observation of the Ge isotope effect, but the continuum which occurs here in the discharge obscures them on our spectrograms. It is therefore not surprising that comparison with our table 2 reveals only one such observation common to the two investigations. Sen Gupta erroneously gives ρ as 1·00582 (instead of 1·00507) for ^{70}GeO, and in consequence the agreement between his observed and calculated displacements for this isotope is not, in fact, quite as close as it appears to be in his table 3.

Sen Gupta, like Shaw and ourselves, is inclined to attribute the system to a $^1\Pi \rightarrow {}^1\Sigma$ transition (as in CO and SiO) rather than to a $^1\Sigma \rightarrow {}^1\Sigma$ transition (as in SnO and PbO), and from a consideration of the estimated energies of dissociation he concludes that both upper and lower states of the emitter are derived from the unexcited states of Ge and O, namely $4s^2\,4p^2\,{}^3P$ and $2s^2\,2p^4\,{}^3P$.

It is fortunate that, since two different sources have been used and the ways in which the results have been discussed are also different, the two investigations, so far from being a case of needless overlapping, may be regarded as usefully complementary.

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ULTRA-VIOLET BAND SYSTEMS OF SnBr AND SiBr

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Received 25 *June* 1937

ABSTRACT. The ultra-violet systems of SnBr and SiBr, as developed in heavy-current tube-discharges through continuous flows of $SnBr_4$ and $SiBr_4$ vapours, are investigated in relation to those of other monohalides of group IV (*b*). For SnBr there are two systems:

(*a*) at λλ3428–3021, of bands degraded towards the further ultra-violet,

$$\nu_{\text{head}} = \left\{ \begin{matrix} 33094{\cdot}5 \\ 30627{\cdot}5 \end{matrix} \right\} - (247{\cdot}1v'' - 0{\cdot}62v''^2);$$

(*b*) at λλ3709–4255, of bands degraded towards the red,

$$\nu_{\text{head}} = \left\{ \begin{matrix} 26654{\cdot}3 + (162{\cdot}3v' - 6{\cdot}8v'^2) \\ 24557{\cdot}9 + 163{\cdot}6v' \end{matrix} \right\} - (247{\cdot}1v'' - 0{\cdot}62v''^2).$$

These appear to be the analogues of the $^2\Sigma \rightarrow {}^2\Pi$ and $^2\Delta \rightarrow {}^2\Pi$ systems, respectively, of SnCl. The electronic separation in the common $^2\Pi$ state is 2467 $cm.^{-1}$, and that in the $^2\Delta$ state is 371 $cm.^{-1}$ Matters of doubt or difficulty in the analysis are discussed.

Miescher's analysis of the SiBr system is modified to include a few hitherto unobserved band-heads and to conform to the doublet transition $^2\Sigma \rightarrow {}^2\Pi$ suggested by analogy to the SiCl and GeBr systems. The more probable of two expressions representing the new measurements is

$$\nu_{\text{head}} = \left\{ \begin{matrix} 33571{\cdot}0 \\ 33153{\cdot}0 \end{matrix} \right\} + (573{\cdot}6u' - 3{\cdot}1u'^2) - (425{\cdot}4u'' - 1{\cdot}5u''^2),$$

where $u = v + \frac{1}{2}$, and the electronic separation in the $^2\Pi$ state is 418 $cm.^{-1}$ The values of the constants for the $^2\Pi$ ground states and $^2\Sigma$ excited states of the monochlorides and monobromides of group IV (*b*) are studied graphically.

§ 1. INTRODUCTION

BAND-SYSTEMS of monohalides of group-IV (*b*) elements have been the subject of several recent investigations, which are summarized in a paper in these *Proceedings*⁽¹⁾ recording the discovery and analysis of ultra-violet emission systems of GeCl and GeBr. These latter resemble the λ2924 system of SiCl⁽²⁾ and the λ2973 system of SnCl⁽³,⁴⁾ and there seems little doubt that they are due to the same transitions, namely $^2\Sigma \rightarrow {}^2\Pi$, the lower ($^2\Pi$) state being the ground state of each of these four emitters. The same interpretation is indicated by recent analyses of the least refrangible (λ4241) system of SiF⁽⁵⁾ and the CCl system near λ2788⁽⁶⁾.

In contrast to these six cases of a $^2\Pi$ ground state are four in which the vibrational analysis of the band-system indicated a single electronic level in the ground state but afforded no information as to the nature of the level, which must presumably be $^2\Sigma$, $^2\Pi_{\frac{1}{2}}$ or $^2\Pi_{1\frac{1}{2}}$. Further investigations appear to be necessary to establish the existence or non-existence of a second electronic level which would complete a $^2\Pi$ ground state. In three of the four cases, namely those of PbF, PbCl and PbBr(7, 8) a search for near infra-red subsystems in emission seems desirable, as has previously been pointed out(1). In the remaining case, however, namely that of SiBr, a solution is to be sought, as will be made clear presently (§ 4), in a reinvestigation of the ultra-violet emission system discovered and analysed by Miescher(9).

The band spectra of two other emitters of this subgroup, namely SnBr and SnI, have been sought by Howell and Rochester(10) in high-frequency discharges through externally heated tubes having external electrodes and containing stannic bromide and stannic iodide, respectively. In the case of the bromide the observed spectrum consisted of a very strong continuum beginning at λ6500 and ending abruptly at λ4400, a set of diffuse bands in the region λ4400–λ3750 followed by a continuum with a maximum at λ3600, and another set of diffuse bands whose resemblance to some bands of the λ2973 system of SnCl suggested that they might be due to a chloride impurity. Analysis of the spectrum could not proceed until a comparison with the bromine emission spectrum had been made. No further data were published. In the case of the iodide a similar spectrum was observed, consisting of a visible continuum, diffuse bands from λ4900 onwards with sharp heads at λλ4350 and 4150, and the iodine continuum near λ3460.

In the present paper the SnBr and SiBr band systems are dealt with, and there remain to be investigated those of CF, GeF, SnF, CBr and all five monoiodides.

§ 2. EXPERIMENTAL

A heavy-current tube-discharge through a continuous flow of the tetrabromide vapour was used as the source for each series of observations. Tin tetrabromide was prepared by direct action of bromine on pure metallic tin; the resulting liquid was distilled from the residual tin and the fraction boiling at 200–207° C. was collected (M.P. 30° C.). The preparation of silicon tetrabromide was effected by the passage of a slow current of nitrogen saturated with bromine vapour over purified silicon maintained at a bright red heat; the colourless condensate was purified by distillation in an all-glass apparatus, the fraction of B.P. 153° C. being collected.

The discharge tubes previously used for germanium tetrachloride and tetrabromide, and shown in figure 1 of the earlier paper(1), were again employed. The only modification necessary was that in the case of tin tetrabromide a pyrex bulb containing the substance was sealed directly on to the pyrex inlet of the discharge tube in place of the soda-glass trap T_1, the stopcock B_1 and the adjacent picein joint having to be dispensed with on account of the higher temperatures to which the substance had to be raised in order to maintain the flow into the discharge tube. The transformer and electrical circuit were also the same as in the previous work.

For the investigation of SnBr a quartz spectrograph (Hilger's E 2 size, dispersion 24–17 A./mm. in the range λ3420–λ3020) and the stronger first order of a 2·4 m. concave grating in an Eagle mounting (dispersion 7·4 A./mm.) were used, Ordinary plates being exposed for 15 and 30 min. in the former instrument and for 2, 3½ and 5 hr. in the latter. A quartz Littrow spectrograph (Hilger's E 1, dispersion 6·0–4·3 A./mm. in the range λ3233–λ2875) was employed for the reinvestigation of the ultra-violet system of SiBr, which was well recorded on an Ordinary plate exposed for 25 min. Miescher⁽⁹⁾ had used an electrodeless discharge in a tube containing silicon tetrabromide vapour, and a three-prism quartz spectrograph of much smaller dispersion (about 15 A./mm. at λ3000).

§ 3. TWO BAND-SYSTEMS OF SnBr

Predictions. For SnBr we may expect to find a $^2\Sigma \rightarrow {}^2\Pi$ system analogous to the SnCl and GeBr systems which have 0 → 0 bands at λλ3198, 2973 and λλ3094, 2988 respectively, and a $^2\Delta \rightarrow {}^2\Pi$ system analogous to the SnCl system whose 0 → 0 band is at λλ3761, 3487. Useful guidance in the detection and analysis of such systems is to be obtained from a study of the trends of the electronic and vibrational constants for SnCl, GeBr and PbBr as shown in tables 5 and 6 of the previous paper⁽¹⁾ and the additional data for SnCl tabulated in Appendix II of the *Physical Society's Report*⁽¹¹⁾. The information so derived may briefly be set out as a number of conditions to be satisfied by the coefficients for the three predicted electronic states of SnBr, thus:

$^2\Pi$ ground state:

(*a*) $1150\ (\mathrm{GeBr}) < 2360\ (\mathrm{SnCl}) < \delta\nu_e\ (\mathrm{SnBr})$.

(*b*) $353{\cdot}6\ (\mathrm{SnCl}) > 296{\cdot}6\ (\mathrm{GeBr}) > \omega_e''\ (\mathrm{SnBr}) > 207{\cdot}5\ (\mathrm{PbBr})$.

$^2\Sigma$ excited state:

(*c*) $33582{\cdot}6\ (\mathrm{SnCl}) > 33443{\cdot}4\ (\mathrm{GeBr}) > \nu_e\ (\mathrm{SnBr}) > 20856{\cdot}8\ (\mathrm{PbBr})$.

(*d*) $432{\cdot}5\ (\mathrm{SnCl}) > 383{\cdot}7\ (\mathrm{GeBr}) > \omega_e'\ (\mathrm{SnBr}) > 152{\cdot}5\ (\mathrm{PbBr})$.

$^2\Delta$ excited state:

(*e*) $28665\ (\mathrm{SnCl}) > \nu_e\ (\mathrm{SnBr})$.

(*f*) $274\ (\mathrm{SnCl}) < \delta\nu_e\ (\mathrm{SnBr})$.

(*g*) $301\ (\mathrm{SnCl}) > \omega_e'\ (\mathrm{SnBr})$.

The direction of degradation of the bands in the two expected systems of SnBr is not indicated unambiguously by these numerical conditions, although analogy with SnCl suggests that it will be towards the further ultra-violet in the $^2\Sigma \rightarrow {}^2\Pi$ system and towards the red in the $^2\Delta \rightarrow {}^2\Pi$.

The $^2\Sigma \rightarrow {}^2\Pi$ *system*. In the stannic bromide discharge the simplest, though not the strongest, molecular feature is a pair of progressions of bands degraded towards shorter wave-lengths in the region λ3428–λ3021, as shown in figure 1(*a*). They are presumably the bands which Howell and Rochester[(10)] described as diffuse and regarded as being possibly due to a chloride impurity. These progressions are accompanied by a continuum, not mentioned by Howell and Rochester, extending from about λ2950 to the strong Sn lines λλ2863·32, 2850·61, 2839·99, and having its intensity maximum near the Sn line λ2913·54. Band-head data (to six significant figures) for these progressions from a grating spectrogram are presented in tables 1(*a*) and 2(*a*), which also include data (given to five significant figures) for three heads measured in a quartz prism spectrogram only. It cannot but be of significance that, if regarded as the $v'=0$ progressions of a doublet system, these

Table 1. SnBr band-heads

(*a*) $^2\Sigma \rightarrow {}^2\Pi$ system; bands degraded to further ultra-violet

v', v''	Subband (ii)			Subband (i)		
	λ_{air}	Int.	$\nu_{vac.}$	λ_{air}	Int.	$\nu_{vac.}$
0, 0	3021·09	4	33091·0	3263·74	*	30621·5
0, 1	43·58	7	32846·5	90·40	7	30382·7
0, 2	66·42	6	32601·9	3317·22	6	30137·1
0, 3	89·23	5	32361·2	44·56	5	29890·7
0, 4	3112·25	4	32121·8	72·02	4	29647·3
0, 5	35·9	2	31880	98·96	2	29412·4
0, 6	59·0	1 ?	31646	3426·3	1 ?	29178

(*b*) $^2\Delta \rightarrow {}^2\Pi$ system; bands degraded to red

v', v''	Subband (ii)			Subband (i)		
	λ_{air}	Int.	$\nu_{vac.}$	λ_{air}	Int.	$\nu_{vac.}$
3, 0	3691·31	0†	27083·0			
2, 0	3709·47	2	26950·4			
3, 1	24·81	1 ?	26839·4			
1, 0	29·37	6	26806·6	4043·95	4	24721·3
2, 1	43·66	5	26704·3			
0, 0	50·84	8	26653·2	70·66	10	24559·1
1, 1		‡		84·70	3	24474·7
0, 1	85·83	7	26406·8	4112·10	10	24311·6
1, 2	98·41	7	26319·5	25·82	5	24230·8
0, 2	3820·78	6*n*	26165·3	53·88	8	24067·1
1, 3	33·74	6	26076·8	67·58	4	23988·0
2, 4	48·89	4	25974·2			
0, 3	57·24	3§	25918·0	96·47	6	23822·8
1, 4	69·56	5	25835·4	4211·10	3	23740·1
2, 5	85·02	4	25732·6			
0, 4				40·37	3	23576·2
1, 5	3906·90	5	25588·4	54·57	1 ?	23497·5
0, 5						
1, 6	44·52	3 ?	25344·6			

Notes:

? Doubtful head.

* Suspected band-head obscured by Sn line λ3262·33, ν30644·1; measure unreliable.

† May be head of SnO band, 0→3.

‡ Subband present but head obscured by atomic line. *n*, nebulous and difficult to locate exactly.

§ Atomic line superposed; measure probably faulty.

progressions give electronic and vibrational separations which satisfy the above requirements, (*a*) and (*b*), of a $^2\Pi$ ground state of SnBr. It will be convenient to refer to the subsystems of lower and higher wave-numbers as (i) and (ii) respectively, as in the case of the GeCl and GeBr systems (1).

With the numeration shown in the tables, the band-heads are represented approximately by

$$\nu=\left\{\begin{matrix}33094\cdot5\\30627\cdot5\end{matrix}\right\}-(247\cdot1v''-0\cdot62v''^2).$$

Unfortunately the values of v'' cannot be settled beyond doubt, because the strong Sn line $\lambda 3262\cdot33$, $\nu 30644\cdot1$, falls very near the head of a suspected subband which, if real, is the 0 → 0 (i), the first measurable head of this progression being the 0 → 1 (i). The existence of the suspected subband has been assumed;* it was suggested by a study of microphotometer traces of a quartz spectrogram, and a rough measure of its head was attempted in a grating spectrogram. Analogy with the case of SnCl suggests that the whole of the difference, 2467 cm.$^{-1}$, of the independent coefficients in this expression represents the electronic interval in the lower ($^2\Pi$) state. This implies an upper state with a single $v'=0$ level 33094·5 cm.$^{-1}$ above the lower $v''=0$ level of the ground state, and it is significant that this satisfies

Table 2. SnBr band-heads (see notes under table 1)

(*a*) $^2\Sigma \rightarrow {}^2\Pi$ system

(ii) $v'=0$	33091·0	244·5	32846·5	244·6	32601·9	240·7	32361·2	239·4	32121·8	242	31880	232	? 31648
	2469·5		*2463·8*		*2464·8*		*2470·5*		*2474·5*		*2468*		*2470*
(i) $v'=0$	* 30621·5	238·8	30382·7	245·6	30137·1	246·4	29890·7	243·4	29647·3	236·9	29412·4	234	? 29178
(*b*) $^2\Delta \rightarrow {}^2\Pi$ system													
(ii) $v'=3$	† 27083·0	243·6	? 26839·4										
	132·6		135·1										
$v'=2$	26950·4	246·1	26704·3						25974·2	241·6	25732·6		
	143·8								138·8		144·2		
$v'=1$	26806·6		‡		26319·5	242·7	26076·8	241·4	25835·4	246·9	25588·4	243·9	25344·6?
	153·4				154·2		158·8						
$v'=0$	26653·2	246·4	26406·8	241·5	26165·3	247·3	25918·0 §						
	2085·4 *2094·1*		— *2095·2*		*2088·7* *2098·2*		*2088·8* *2095·2*		*2095·3* —		*2090·9*		
(i) $v'=1$	24721·3	246·6	24474·7	243·9	24230·8	242·8	23988·0	247·9	23740·1	242·6	23497·5 ?		
	162·2		163·1		163·7		165·2		163·9				
$v'=0$	24559·1	247·5	24311·6	244·5	24067·1	244·3	23822·8	245·6	23576·2				
$v''\rightarrow$	0		1		2		3		4		5		6

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* If no such assumption were made, and the first measured head of the progression were taken to be the 0→0 (i), the electronic separation would be about 2710 cm.$^{-1}$ instead of 2467, and the values of the vibrational coefficients would be slightly different from those in the above formula.

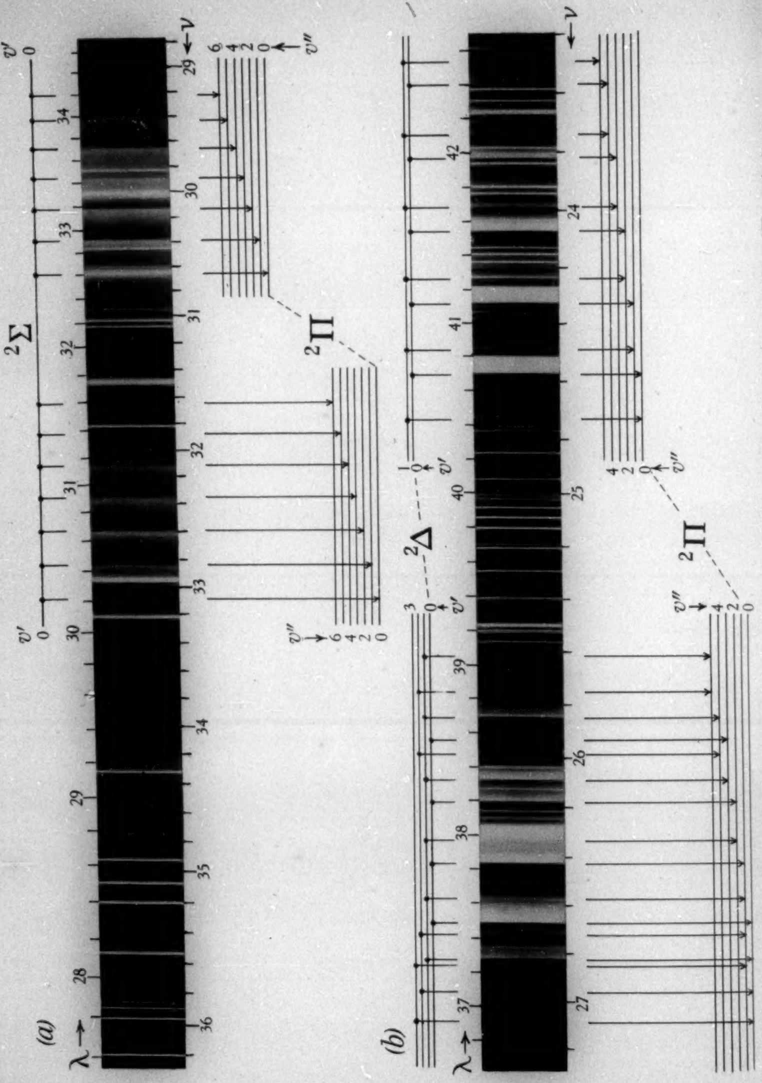
(a)
(b)
λ →
← ν
²Σ
²Π
²Δ
v′
v″
0
2
4
6
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
24
25
26
27

Figure 1. SnBr band systems: (a) λ3021 system, $^2\Sigma \rightarrow {}^2\Pi$ (quartz prism); (b) λ3751 system, $^2\Delta \rightarrow {}^2\Pi$ (grating).

To face page 559

one requirement (*c*) of the $^2\Sigma$ state of SnBr. Although no vibrational levels are observed for the upper state, it is probable that the remaining condition (*d*) is also fulfilled, since the direction of degradation indicates that ω_e' exceeds ω_e'', which is 247·7 cm.$^{-1}$, and in a later section (§ 5) it will be shown that ω_e' would probably be of the order 300 cm.$^{-1}$ It would appear, then, that these two progressions belong to a $^2\Sigma \rightarrow {}^2\Pi$ system.

The $^2\Delta - {}^2\Pi$ *system.* More prominent, but less simple, features of the discharge spectrum are two subsystems of bands degraded towards the red in the region λ3709–λ4255. Some of these may, perhaps, be identical with some of Howell and Rochester's diffuse bands between λλ3750 and 4400, for which no data were published. A grating spectrogram of this region is reproduced in figure 1(*b*), and the band-head data obtained from it are set out in tables 1(*b*) and 2(*b*). It is at once evident that the v'' progressions in each of the subsystems now under consideration have the same vibrational intervals as the two progressions considered above. These subsystems therefore involve the same lower state, $^2\Pi$.

Further, the two prominent v'' progressions with $v'=0$ are separated from one another by about 2096 cm.$^{-1}$ The difference, 371 cm.$^{-1}$, between this and the electronic interval, 2467, in the $^2\Pi$ state may be interpreted as the electronic interval in the upper state.* As such it will satisfy one of the above requirements (*f*) of a $^2\Delta$ state of SnBr corresponding to the upper state of the $^2\Delta \rightarrow {}^2\Pi$ system of SnCl(4, 11). The position of the 0 → 0 (ii) subband, ν26653·2, which gives the energy of one of the $v=0$ levels of the upper state relative to that of the ground state, satisfies a further requirement (*e*) of the $^2\Delta$ state.

As to the remainder of the analysis shown in table 2(*b*), while no special difficulty is encountered in the more refrangible subsystem (ii), a little uncertainty remains in the case of the less refrangible (i). The latter consists of a progression of very strong and narrow bands ($v'=0$) and a progression of relatively weaker bands; and so marked is the difference of appearance in the two progressions, that some hesitation is felt in interpreting the weaker as the $v'=1$ progression of the same subsystem (i). The doubt is increased by the fact that the resulting mean value, 163·6 cm.$^{-1}$, of the vibrational interval $\omega_{\frac{1}{2}}$ is considerably greater than that in the other subsystem (ii), namely 155·5 cm.$^{-1}$ This inequality is not, of course, a fatal objection, since many cases of a discrepancy between the vibrational coefficients derived from measurements (mostly band-head measurements) in a pair of subsystems have been recorded, as will be seen in Appendix II of this Society's *Report*(11); e.g. in the $^2\Pi$ and $^2\Delta$ states of the analogous emitter SnCl, and in $^2\Pi$ states of ScO, YO, LaO, CaF, SrF, BaF, NO and NS. Only in the last-named case, however, is the discrepancy as great as (it is actually much greater than) the one mentioned here.

The band-heads are approximately represented by

$$\nu = \left\{ \begin{matrix} 26654{\cdot}3 + (162{\cdot}3v' - 6{\cdot}8v'^2) \\ 24557{\cdot}9 + \;163{\cdot}6v' \end{matrix} \right\} - (247{\cdot}1v'' - 0{\cdot}62v''^2).$$

---

* If the electronic interval in the $^2\Pi$ ground state were taken as 2710 cm.$^{-1}$ in accordance with the preceding footnote (p. 558), the interval in this upper state would be 2710 − 2096 = 614 cm.$^{-1}$, which would also fulfil the condition (*f*) for the predicted $^2\Delta$ state of SnBr.

The function of v'' is identical with that in the expression for the $^2\Sigma \rightarrow {}^2\Pi$ system, since the data for both systems have been used together in the derivation of the coefficients of v'' and v''^2. It should be pointed out that although the value of ω'_e remains rather uncertain the observed vibrational intervals in the upper state satisfy the remaining requirement (*g*) of a $^2\Delta$ state of SnBr, and there appears to be ample reason for regarding this system as the expected $^2\Delta \rightarrow {}^2\Pi$, in spite of the difficulties to which attention has been drawn.

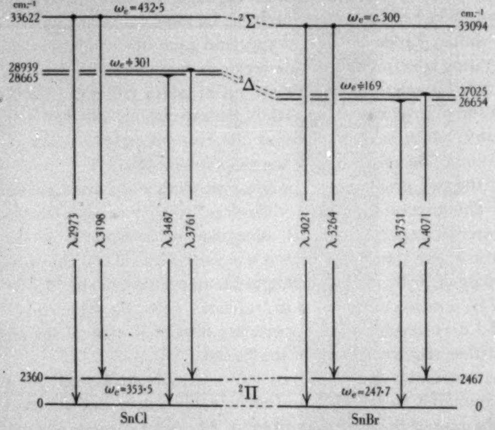

Figure 2. Electronic energy levels and band systems of SnCl and SnBr. The energies given are for the $v=0$ levels. The rough estimate of ω_e for the $^2\Sigma$ state of SnBr is obtained from figure 4, and not from direct measurement of band heads.

Tables 1 (*b*) and 2 (*b*) exclude a few observed heads (mostly weak or doubtful) for which no place is found in this system. Some of the subbands (ii) appear to have second heads with wave-numbers from 2·5 to 5·0 cm.⁻¹ higher than those of the heads tabulated. Some of the second heads, if real, have displacements of the same order as those in the Br isotope effect, $0{\cdot}0075\,(\nu-\nu_e)$, but others certainly cannot be so interpreted.

The peculiar appearance of the strong narrow subbands (i) referred to above is shown to some extent in the reproduction, figure 1 (*b*), but far more detail is seen in microscopic examination of the grating spectrograms. Thus the strong subband at λ4070·66 extends only as far as an abrupt edge at λ4080·54 and also has between these limits other edges or heads separated by sharp minima at λλ4076·0 and 4078·5. Similarly the neighbouring strong subband whose head is at λ4112·10 ends abruptly at λ4121·45 and has two minima; and the next two extend only from λ4153·88 to λ4155·96 and from λ4196·47 to λ4199·64 respectively. In each case the long-λ edge of the subband simulates a head degraded in the short-λ direction.

In the region (omitted from figure 1) between the two SnBr systems, the spectrograms show the continuum observed by Howell and Rochester (maximum near $\lambda 3600$). Superposed on this continuum are the unquenched $0 \rightarrow 1$ and $0 \rightarrow 2$ bands of SnO near $\lambda 3484$ and $\lambda 3585$(12), and it is possible that the $0 \rightarrow 3$ band near $\lambda 3691$ is also present (see note † under table 1).

Vibrational energy level diagrams of the two SnBr systems are included in figure 1, and the electronic energy level diagram of SnBr is compared with that of SnCl in figure 2.

§ 4. A REINVESTIGATION OF THE SiBr BAND-SYSTEM

In view of the fact that seven of the eight analysed band spectra of monohalides of C, Si, Ge and Sn are now known to involve doublet lower states, which are almost certainly $^2\Pi$ ground states, the apparently exceptional case of SiBr needs careful examination. The order of magnitude of the electronic separation to be expected in the ground state of SiBr can roughly be estimated from a consideration of the separations, $\delta\nu_e$, as set out in table 5 of the earlier paper(1). It should be (*a*) larger than that in SiCl (208 cm^{-1}), (*b*) very much smaller than that in GeBr (1150), as is suggested by the ratio of the SiCl and GeCl separations (208 : 975), and (*c*) perhaps less than one-half of that in GeCl (975) as is suggested by the ratio of the GeBr and SnCl separations (1150 : 2360). It may accordingly be expected to lie between the limits 350 and 450 cm^{-1}

Miescher(9) represented the band-heads in the ultra-violet system of SiBr by

$$\nu = 33570 + (578 \cdot 3u' - 4 \cdot 3u'^2) - (424 \cdot 6u'' - 1 \cdot 3u''^2),$$

where $u = v + \frac{1}{2}$. There seems to be no doubt that this is the system in which some indication of a $^2\Pi$ lower state with an interval of the above order of magnitude should be sought, for in every other respect the values of the constants satisfy the obvious requirement that they should fall between those of the constants for SiCl and GeBr, namely, $\nu_e = 34102 \cdot 7$ and $33443 \cdot 4$ respectively, $\omega_e'' = 535 \cdot 4$ and $296 \cdot 6$, $x_e''\omega_e'' = 2 \cdot 20$ and $0 \cdot 9$, and $\omega_e' = 700$ (approximately) and $383 \cdot 7$.

It will be seen that the intervals between the vibrational levels of the lower state are of the same order of magnitude as the expected electronic separation; and it is possible that this fact might account for the non-detection, with the comparatively small dispersion used by Miescher, of band-heads belonging to the missing subsystem. This might well be the case if the electronic separation happened to be not more than, say, 5 cm^{-1} greater or less than one of the vibrational intervals $\omega_{\frac{1}{2}}''$, $\omega_{1\frac{1}{2}}''$, $\omega_{2\frac{1}{2}}''$, which the above formula gives as $422 \cdot 0$, $419 \cdot 4$, $416 \cdot 8$ cm^{-1} respectively.

Dispersion roughly three times that used by Miescher has been employed in obtaining new band-head data, which are shown in tables 3 and 4. The heads detected with certainty are slightly less numerous than those listed by Miescher, but they include a few additions which indicate that his analysis, although the best attainable with the low-dispersion data used, needs a slight but important modification. The 0 → 2, 0 → 1 and 1 → 1 heads in Miescher's analysis are now measured as close doublets, with separations of 4·0, 3·6 and 5·0 cm.$^{-1}$, respectively; and the 0 → 3 head also appears to be a doublet with an even smaller separation. These doublets cannot be satisfactorily interpreted as *P*-form and *Q*-form heads of the bands mentioned, since no corresponding doubling is found in the 0 → 0 band. Nor can they be explained by the Br isotope effect, as the isotopic displacements 0·00325 $(\nu - \nu_e)$ at the positions of these heads are 2·5, 1·1 and 0·7 cm.$^{-1}$ respectively, and (except perhaps the first) would be too small for measurement.* Moreover, the

Table 3. SiBr band-heads

Miescher				Authors				
v', v''	λ_{air}	Int.	$\nu_{\text{vac.}}$	v', v''	Sub-band	λ_{air}	Int.	$\nu_{\text{vac.}}$
1, 8	3233·6	2	30916	1, 8	(ii)	3233·34	0*n*	30918·9
2, 9	17·4	2	31072	2, 9	(ii)	17·27	1	31073·3
1, 7	3192·0	4	319	1, 7	(ii)	3192·38	3	315·6
2, 8	76·3	4	474	2, 8	(ii)	75·46	4	482·4
0, 5	67·5	5	562	0, 5	(ii)	67·49	5	561·6
				1, 5	(i)	52·45	6 ?	712·4 }
1, 6	51·7	6	720	1, 6	(ii)	51·68	6	720·0 }
2, 7	36·0	4	879	2, 7	(ii)	36·96	6 ?	868·8
0, 4	26·6	7	974	0, 4	(ii)	26·63	8	974·1
1, 5	11·3	7	32132	1, 5	(ii)	11·55	8	32129·0
2, 6	3096·7	4	283	2, 6	(ii)	3096·46	4 ?	285·6
0, 3	86·9	8	386	0, 3	(ii) }	86·78	10*d*	386·8
				0, 2	(i) }			
1, 4	72·2	7	541	1, 4	(ii)	72·31	9	539·5
2, 5	57·6	3	696	2, 5	(ii)	58·01	4 ?	691·5
0, 2	47·5	9	804	0, 2	(ii)	47·68	20	802·3 }
				0, 1	(i)	47·31	20	806·3 }
1, 3	33·4	6	957	1, 3	(ii)	33·65	12	954·0
				0, 1	(ii)	09·17	15	33222·1 }
0, 1	08·8	10	33226	0, 0	(i)	08·84	25	225·7 }
1, 2	2995·0	5	379	1, 1	(i)	2995·69	6*n*	371·6
2, 3	82·3	4	521					
0, 0	71·2	6	647	0, 0	(ii)	71·29	8	645·6
				1, 1	(ii)	58·73	10	788·5 }
1, 1	58·3	7	793	1, 0	(i)	58·29	10	793·5 }
2, 2	45·7	5	938					
1, 0	21·8	8	215	1, 0	(ii)	21·98	10	34213·3
2, 1	10·3	4	351	2, 1	(ii)	10·25	5 ?	351·3
2, 0	2874·9	4	774	2, 0	(i)	2874·96	2	772·9

? Doubtful head.
n, nebulous and difficult to locate exactly
d, probably double, but not measured as such on account of an atomic line.

---

* No band-heads attributable to the Br or the Si isotope effect have been measured, with the possible exception of a doubtful one at λ2922·25, ν34210·2, which may be the ^{28}Si^{81}Br head of the 1 → 0 subband (ii) if the head at ν34213·3 in tables 3 and 4 is attributed to the equally abundant emitter ^{28}Si^{79}Br, the observed and calculated displacements being 3·1 and 2·1 cm.$^{-1}$ respectively. Observation of the isotope effects is expected to be rendered more difficult and unreliable by the doubling of heads due to the near equality of the electronic and vibrational separations discussed in this section.

additional heads appear to be quite genuine and cannot be ignored as fortuitous blends of rotational structure lines. It therefore seems reasonable to accept them as indications of the missing subsystem; and, as table 4 shows, they can be included in either of two alternative arrangements of this part of a doublet system, both of which are presented since neither appears to be markedly inferior to the other.

Table 4. Two possible arrangements of a part of the SiBr doublet system

(*a*)

↑ v′	v″ →	0		1		2		3		4		5
2	(ii)	34772·9	421·6	34351·3								32691·5
	(i)	—		—								—
		559·6		557·8								562·5
		—		—								—
1	(ii)	34213·3	419·8	33793·5	421·9	33371·6	417·6	32954·0	414·5	32539·5	410·5	32129·0
		424·8										
	(i)	33788·5		—		—		—		—		—
		567·7		567·8		565·3		567·2		565·4		567·4
		566·4		—		—		—		—		—
0	(ii)	33645·6	419·9	33225·7	419·4	32806·3	419·5	32386·8	412·7	31974·1	412·5	31561·6
		423·5		*423·4*								
	(i)	33222·1	419·8	32802·3		—		—		—		—

(*b*)

↑ v′	v″	0		1		2		3		4		5
2	(ii)	34772·9	421·6	34351·3								32691·5
	(i)	—		—								—
		559·6		562·8								562·5
		—		—								—
1	(ii)	34213·3	424·8	33788·5				32954·0	414·5	32539·5	410·5	32129·0
		419·8		*416·9*								*416·6*
	(i)	33793·5	421·9	33371·6				—		—		31712·4
		567·7		566·4				567·2		565·4		567·4
		567·8		565·3				—		—		—
0	(ii)	33645·6	423·5	33222·1	419·8	32802·3	415·5	32386·8	412·7	31974·1	412·5	31561·6
		419·9		*415·8*		*415·5*						
	(i)	33225·7	419·4	32806·3	419·5	32386·8		—		—		—

In table 4(*a*) the three components of slightly *larger* ν are regarded as the 0 → 2, 0 → 1 and 1 → 1 heads in the more complete subsystem (ii), and those of slightly *smaller* ν as the 0 → 1, 0 → 0 and 1 → 1 heads in the hitherto undetected subsystem (i). With this interpretation the band-heads of the whole system are approximately represented by the expression given in a preliminary note(13), namely

$$\nu = \begin{Bmatrix} 33571{\cdot}2 \\ 33147{\cdot}2 \end{Bmatrix} + (574{\cdot}8u' - 4{\cdot}0u'^2) - (424{\cdot}7u'' - 1{\cdot}4u''^2).$$

This gives 424 cm.$^{-1}$ as the electronic interval in the lower ($^2\Pi$) state, and, apart from the inclusion of the smaller of the two independent coefficients, differs but slightly from Miescher's expression.

In table 4(*b*) the quantum numerations of the components of each of the three observed doublets are interchanged, so that the *smaller-ν* components become the 0 → 2, 0 → 1 and 1 → 1 heads in subsystem (ii), and the *larger-ν* components the 0 → 1, 0 → 0 and 1 → 0 heads in subsystem (i). A single head is transposed from 1 → 2 (ii) to 1 → 1 (i); another head, suspected to be a close doublet but not measured as such, appears not only as 0 → 3 (ii) but also as 0 → 2 (i) (this is quite reasonable but is numerically unsatisfactory in table 4(*a*)); and another probable head, hitherto unallocated, finds a place as 1 → 5 (i). With this arrangement, the band-heads are approximately represented by

$$\nu=\left\{\begin{matrix}33571{\cdot}0\\33153{\cdot}0\end{matrix}\right\}+(573{\cdot}6u'-3{\cdot}1u'^2)-(425{\cdot}4u''-1{\cdot}5u''^2),$$

and the estimate of the electronic interval in the lower ($^2\Pi$) state is rather lower, namely 418 cm.$^{-1}$

The v', v'' numbering for the latter arrangement, which a study of the vibrational separations seems to indicate as the more satisfactory of the two, is provisionally adopted and also included in table 3. Whichever arrangement is adopted there is no longer any reason to regard SiBr as an exceptional case in which the ground state is single rather than a $^2\Pi$ state with an electronic separation of the expected order of magnitude.

An examination of the intensities of the bands supports this conclusion; for both in the reproduction published by Miescher and also in the new spectrograms Miescher's 0 → 2, 0 → 1 and 1 → 1 bands appear to be abnormally strong in comparison with his 0 → 0 band, the reason being, according to the present interpretation, that another subband is superposed on each of them.

The numerical results of this study were included, for the sake of completeness, in tables 5 and 6 of the earlier paper(1).

§ 5. $^2\Pi$ AND $^2\Sigma$ STATES OF GROUP-IV(*b*) MONOCHLORIDES AND MONOBROMIDES

In another recent paper in these *Proceedings*(14), on the ultra-violet band-system of GeO, the available data for certain band-systems of the monoxides and monosulphides of group-IV(*b*) elements were studied graphically. Both for the ground states and also for the excited states in the selected systems, many of which are known to be $^1\Pi \rightarrow {}^1\Sigma$, the decrease of each of the vibrational coefficients ω_e and $x_e\omega_e$ with the increase of the number of electrons in the molecule follows an uninflected curve, while no such smoothness is shown by the decrease of electronic energy ν_e of the upper state.

Of the spectroscopic investigations of the monohalides of this subgroup only those of the monochlorides and monobromides are sufficiently complete for a similar graphical test to be applied. As $^2\Delta \rightarrow {}^2\Pi$ systems are known for only SnCl and SnBr, the test must be restricted to the $^2\Sigma \rightarrow {}^2\Pi$ systems and the PbCl and PbBr systems, the data for which are collected in tables 5 and 6 of the paper on GeCl and GeBr(1). Further, $x_e\omega_e$ is excluded from the test as in some cases it is either unknown or only roughly estimated.

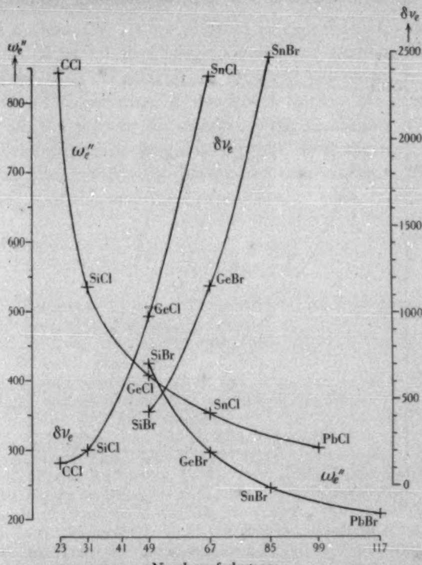

Figure 3. Variations of the electronic separations ($\delta\nu_e$) and vibrational coefficients (ω_e'') in the $^2\Pi$ ground states of monochlorides and monobromides of group-IV (*b*) elements. The numerical values are given in table 5 of a previous paper(1). The tentative results, $\delta\nu_e = 0$, for PbCl and PbBr are omitted.

The results for the lower states are shown in figure 3. For ω_e'' of the chlorides and bromides (including PbCl and PbBr), two uninflected curves are obtained, which are similar in form and disposition to those for ω_e'' of the oxides and sulphides, respectively; the curves intersect between the points for the two iso-electronic pairs of emitters GeCl, SiBr and SnCl, GeBr. A pair of uninflected curves is also obtained for the electronic separation $\delta\nu_e$ in all emitters except PbCl and PbBr, for each of which only a single electronic level has so far been found in the ground state. These regularities seem to support the view that similar states are in fact being compared, and that since some of them are known to be $^2\Pi$ ground states all must be.

Figure 4 shows the results for the upper states, some of which are known to be, and all may be, $^2\Sigma$. In the case of ω_e' the points for all the chlorides except PbCl lie on a curve of the same form as that for the oxides, but in the absence of observational data for CBr and SnBr little can be said of the bromides, except that the intersection of the two ω_e' graphs is similar to that of the two ω_e'' curves in figure 3. The value of ω_e' for SnBr would appear to be of the order 300 cm.$^{-1}$ In the case of the electronic energy ν_e the result is the same as for the oxides and sulphides, no simple curves being obtained; and, moreover, the sudden falls to the points for PbCl and PbBr, considered together with the change in the ω_e' curve beyond SnCl, suggest that the upper states of PbCl and PbBr may not be strictly analogous to those of the other emitters.

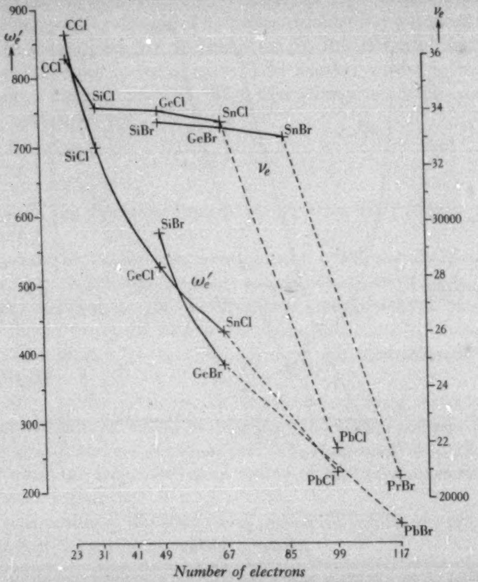

Figure 4. Variations of the electronic energies (subsystem origins ν_e, or wave-numbers of 0→0 subbands) and vibrational coefficients (ω_e') for $^2\Sigma$ excited states of monochlorides and monobromides of group-IV(*b*) elements, probably all analogous states except for PbCl and PbBr. Numerical values are given in table 6 of a previous paper(1).

If, instead of the number of electrons in the molecule, the reduced mass* (μ) is used as abscissa, the graphs obtained are somewhat similar to those in figures 3

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* Values of $10^{24}\mu$ (g.):

CCl	14·78	SiCl	25·83	GeCl	39·29	SnCl	45·02	PbCl	49·92
CBr	17·20	SiBr	34·24	GeBr	62·73	SnBr	78·76	PbBr	95·08

and 4, except that for the chlorides both the ω_e' curve and the ω_e'' curve have inflections between the GeCl and SnCl points. This loss of simplicity of the curves is similar to that previously noticed in the case of the monoxides.

§ 6. ACKNOWLEDGMENTS

One of the authors (W. J.) has pleasure in expressing his indebtedness to the Fereday Electors of St John's College, Oxford, for enabling him to take part in the work, to Prof. G. P. Thomson for excellent laboratory facilities, and to the Government Grant Committee of the Royal Society for grants for apparatus. The other (L. A. B.) records his thanks to the Governors of Collyer's School, Horsham, and the Education Committee of the West Sussex County Council for personal grants. The authors also have pleasure in thanking Prof. H. Dingle for helpful discussions of this and other papers of the series.

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ABSORPTION SPECTRA OF SOME CARBON AND TIN HALIDES IN THE VAPOUR STATE*

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Received 15 *February* 1937

ABSTRACT. The absorption spectra of the vapours of $SnCl_4$, $SnBr_4$ and of molecules of the types CX_4, CHX_3, and CH_2X_2 (X = Cl, Br, I) are investigated. From the number of maxima and their energy differences, and a comparison of the beginnings of the various absorption regions with thermochemical data, it is concluded that the first process of photodissociation corresponds not to the process $MX_4 \rightarrow MX_3 + X$ but to $MX_4 \rightarrow MX_2(^1\Sigma) + 2X$ etc.; the further absorption regions are due to one or two excited halogen atoms.

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§ 1. INTRODUCTION

Recently it has been shown⁽¹⁾ that the photodissociation of polyatomic molecules, formed by atoms of groups V and VI of the periodic table, follows different courses according to the state of valency of the central atom. In lower states of valency, i.e. as long as chemical combination is brought about by the p electrons of the central atom, the bond energies D_B are decisive for the photolytic process. In the state of maximal valency involving the activation of the two electrons of the group s^2, the thermochemical difference D_T of the atomic energy of formation of this molecule and the corresponding one of lower valency determines the decomposition by light. According to Heitler and London's⁽²⁾ conception, the unexcited carbon atom is divalent only from the point of view of a pair-bond theory of valency, and, whichever its partner may be, it becomes tetravalent by excitation to a term of sp^3 or p^4. Accordingly the same ideas should apply to tetrahalides formed by atoms of group IV in their maximal state of valency. We have reinvestigated the absorption spectra of some molecules of this type in the vapour state and present the result in this paper. They lead, as will be seen, to a new interpretation of the photodissociation of simple organic compounds. The products of decomposition by light of a molecule of the type CH_4 are $CH_2 + 2H$, CH_2 being a saturated molecule in a $^1\Sigma$ state which does not possess free valencies as $SnCl_2$, for instance, does. This will lead to a reinterpretation of certain absorption spectra of organic molecules because it shows that the photodissociation sometimes takes place, not through the rupture of a bond according to its adiabatic energy of dissociation, but by the excitation of the molecule to the repulsive excited term involving unexcited radicals and atoms. The energy of such an excitation is generally lower than a true bond energy. The bond energies themselves can then be found from the measured values of D_T. In the present paper, dealing with absorption in the quartz ultra-violet, at first only such bond energies, involving unexcited carbon atoms ($s^2p^2\ {}^3\mathrm{P}$), are investigated.

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* A preliminary report on this subject has been published in *Current Science*.

§ 2. EXPERIMENTAL

The experimental method has been the same as that described earlier; but for some of the substances we took additional plates on a small Hilger quartz spectrograph of exceptionally good transparency, using the positive crater of the carbon arc as a source of light. By means of plates treated with mineral oil we could photograph the spectrum down to λ1950 with a few minutes' exposure. Figures 1–3 show microphotometer records of the spectra of CI_4 and CHI_3 as examples of the ordinary method described earlier and a record of the $CHBr_3$ spectrum as an example of the second method. It will be seen that the instability of the carbon arc and the oiling of the plate, whereby a strong general background is often produced owing to fluorescence on account of scattered light, make this method much less reliable. But while the last absorption limit is rather uncertain and falls just short of the region where the plate becomes entirely blank, the preceding two maxima and limits can be determined quite well. The values finally accepted are the weighted means from several spectrograms.

Some further remarks on the determination of the long-wave limits appear necessary. The first beginning of continuous absorption is never well defined. In $SnCl_4$, for instance, with an absorption cell of length 10 cm. at room-temperature (~25° C.) and a vapour pressure of about 1 mm. of mercury, it is at λ2450 A. With 9 mm. of mercury and a cell of length 80 cm., it reaches 2570 A.; and with the temperature increased to 300° C. and the pressure to 18 mm. of mercury, with the same cell, the limit goes up to 2820 A. This difficulty in the determination of the true long-wave limit for the vibrationless molecule has been discussed by Jan Khan and Samuel⁽¹⁾, and it has been shown that this large red shift is simply due to the absorption from higher vibrational levels of the ground state. The higher the level the less it contributes to the selective absorption, and the contribution of higher levels beyond a particular one according to the particular conditions (length of absorbing layer, temperature, and vapour pressure) will fall below the last value indicated by the photographic plate on account of its threshold value. An increase of any of the above three parameters increases the number of molecules in higher levels, either by an increase of the population of the higher ones at the expense of the lowest or simply by an increase in the absolute number of molecules. A red shift of the first long-wave limit results naturally, but this has no physical meaning for the vibrationless molecule, either as to its dissociation energy, or as to the shape of its potential curve, or as to the character of the bond. Since there appears to be some confusion on this point in the literature, attention may be drawn to two simple experimental facts which establish this interpretation. First,

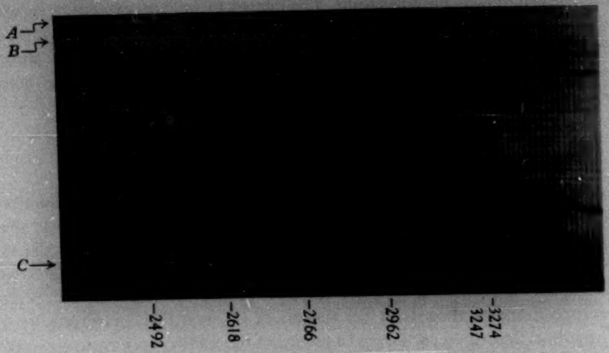

Figure 1. CI_4.

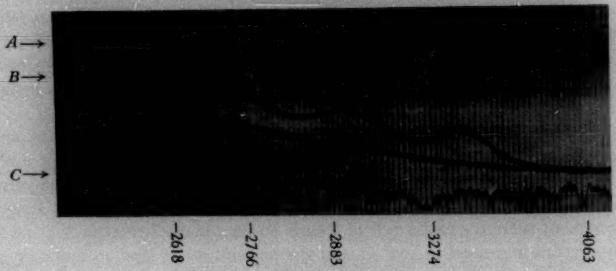

Figure 2. CHI_3.

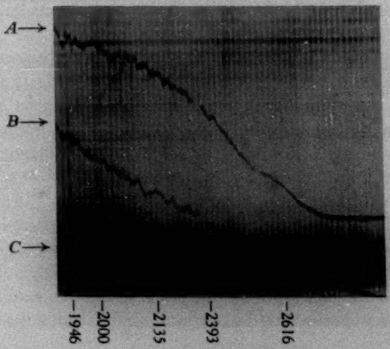

Figure 3. $CHBr_3$.

Microphotometer records of absorption spectra: *A*, absorption spectrum; *B*, source of light; *C*, copper arc.

it can be seen from molecules exhibiting band spectra that the absorption is indeed by no means confined to the vibrationless molecule. For instance, bromine vapour in a layer of 10 cm. and a pressure of about 5–10 cm. exhibits the five lowest vibrational levels of the ground state of Br_2. Again in SO_2 in a 10-cm. cell and pressure of the order of some tenths of a millimeter the first three levels of the symmetric and antisymmetric valence vibration appear. These higher vibrational levels of the ground state are important, not only with regard to the actual energy-difference between the higher and the lowest level, but even more on account of the change of relative position of two potential curves with increase of internuclear distance. Secondly, in certain favourable cases we are able to estimate the beginning of absorption of a continuous spectrum independently of the experimental long-wave limit. If, for instance, a molecule decomposes under the action of light in such a way that in the first region of selective absorption one of the dissociation products is an unexcited Br atom in its ground state $^2P_{\frac{3}{2}}$, and in the second absorption region an excited Br atom ($^2P_{\frac{1}{2}}$), the absorption spectrum will show two maxima whose energy-difference is approximately equal to the term difference $^2P_{\frac{1}{2}}$–$^2P_{\frac{3}{2}}$ of Br, e.g. 3685 $cm.^{-1}$ or about 10·5 kcal./mol. The position of these two maxima will not be influenced very much by the experimental conditions; and the more nearly parallel the two repulsive curves concerned run, the better will the energy difference between the maxima agree with the energy of excitation of the Br atom. The two maxima preserving their wave-lengths, the point of retransmission between them also has a fairly constant wave-length. This latter point is near the beginning of the second absorption region and hence the true long-wave limit of the first absorption region of the vibrationless molecule should be found at a distance towards the red from the point of retransmission which corresponds approximately to the excitation energy of Br($^2P_{\frac{1}{2}}$) or the energy-difference of the two maxima. Obviously, only for one of the many possible values of the first long-wave limit is this necessary condition valid, and empirically this particular value lies rather more often than not in the vicinity of the maximum. As a rule the value of its extinction coefficient is of the order of one-tenth of that of the maximum. Such a value of the first long-wave limit generally appears, e.g., in a 10-cm. absorption tube at room-temperature with a pressure of 1–10 mm. of mercury. Indeed, in recent years wherever a correlation of long-wave limits to photolytic processes has been possible, whether in the case of gases and vapours at room-temperature or even in the experiments of Franck and his collaborators on alkali and silver salts of high melting-points, the first beginning of absorption has, with a number of absorbing molecules generally been found to be roughly equal to that obtaining under the conditions described above, while measurements with absorbing layers of 10 or 30 m. have not led to values related to thermochemically measured energies, and such observations do not concern the vibrationless molecule.

Table 1 displays the wave-lengths of the beginnings and maxima of absorption measured by us under conditions such as those outlined above. They are weighted means from several spectrograms, each measured directly on the microphotometer records.

Table 1

Molecule	First long-wave limit	First maximum	Second long-wave limit	Second maximum	Third long-wave limit	Third maximum
$SnCl_4$	~2500	—	—	—	—	—
$SnBr_4$	3471	3063	2915	2728	2442	—
CI_4	3930	3449	3177	3010	2795	2700
CHI_3	4230	3429	3229	3029	2872	2828
CH_2I_2	3499	2955	2640	2474	2365	2220
CBr_4	2932	2525	2453	—	—	—
$CHBr_3$	2750	2559	2497	2275	2195 (?)	—
CCl_4	~2350	—	—	—	—	—
$CHCl_3$	~2200	—	—	—	—	—

§ 3. SPECTRA OF $SnCl_4$ AND $SnBr_4$

There exists only one molecule of the CH_4 type, i.e. $SnCl_4$, whose energy of formation (Q) is known along with that of the corresponding dihalide $SnCl_2$. Consequently we took this as the starting point. The thermochemical values in kcal./mol. are,* for $SnCl_4$: $Q=126{\cdot}4$, $S(\mathrm{Sn})=69{\cdot}9$, $S(\mathrm{SnCl_4})=9{\cdot}6$, and for $SnCl_2$: $Q=80{\cdot}8$, $S=26{\cdot}7$. By means of Born's cycle we obtain, with $D(\mathrm{Cl_2})=56{\cdot}9$, the values $D(\mathrm{SnCl_4})=300{\cdot}5$ and $D(\mathrm{SnCl_2})=180{\cdot}9$. The difference D_T of these figures is 120 kcal./mol.

The absorption spectrum of $SnCl_4$ has been investigated independently by Sharma(3) and by Hukumoto(4). While the latter records a long-wave limit of continuous absorption at $\lambda 2820$ or 99 kcal./mol., the former finds two regions of absorption with beginnings at $\lambda 3400$ and $\lambda 2750$. We have ascertained that Sharma's first maximum belongs to free Cl_2 molecules.†

With an absorption tube of length 10 cm. and vapour pressure of 1–10 mm. of mercury the beginning of absorption of $SnCl_4$ lies at about $\lambda 2450$ to 2500 A., corresponding to 116 to 114 kcal./mol., i.e. values in agreement with that of D_T calculated from thermochemical data, namely 120 kcal./mol.

This close agreement between D_T and the first long-wave limit of molecules of MX_4 type will be further confirmed by the experimental results set out below. At the present stage it is not necessary to attach too much importance to the actual value, which depends on the pressure in the absorption tube, and it is sufficient to conclude that a long-wave limit, measured under reasonable conditions, does indeed fall near about the region indicated by the energy difference $D(\mathrm{SnCl_4}) - D(\mathrm{SnCl_2})$.

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* All values are taken from Landolt-Boernstein's tables. The procedure and the symbols used are the same as in Jan Khan and Samuel's paper(1).

† It is well known that Cl_2 at low pressures exhibits only the continuous spectrum associated with its band spectrum, on account of the particular position of the potential curve of the excited term; the absorption maximum of this continuous lies at about $\lambda 3350$. Sharma has not recorded the maximum of his first region of selective absorption, but we also obtained it sometimes after a fresh refilling of the apparatus; it disappeared gradually on evacuating and repeated careful washing of the absorption cell with $SnCl_4$ vapour. It can be reproduced by decomposition of the $SnCl_4$ in the side bulb; the saturation pressure of $SnCl_4$ is about 20 mm. of mercury at room temperature, and this maximum appeared always when the manometer shows a pressure of 3–10 cm.

Definite confirmation as to the products of photodissociation have been obtained from the spectrum of $\mathrm{SnBr_4}$. Its heat of formation from the elements is not known, but $Q(\mathrm{SnBr_2})$ is measured as 61·5 kcal./mol. and by estimating S as 22 kcal./mol., we can calculate $D(\mathrm{SnBr_2})$ by means of Born's cycle to be about 160 kcal./mol.

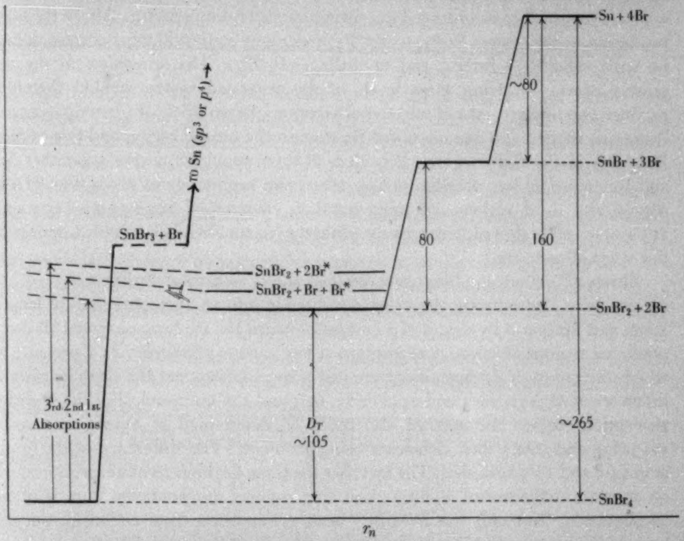

Figure 4. Simplified Franck-Condon diagram of the lower electronic terms of $\mathrm{SnBr_4}$.

The values of $D(\mathrm{SnCl_2})$ and $D(\mathrm{SnCl_4})$ are in the ratio of about 3 : 5, and if such an extrapolation is possible at all, $D(\mathrm{SnBr_4})$ should be 66 per cent greater than $D(\mathrm{SnBr_2})$, i.e. about 265 kcal./mol. Assuming that the photolytic process takes place according to the equation

$$\mathrm{SnBr_4} + h\nu = \mathrm{SnBr_2} + 2\mathrm{Br},$$

we can represent the position of the electronic terms and their dissociation in the simplified Franck-Condon diagram of figure 4, which also will serve as an example for the molecules discussed below. The Sn atom still being in its divalent state, the approach of the two Br atoms towards the $\mathrm{SnBr_2}$ molecule produces a repulsive potential curve without a minimum, the selective absorption of $\mathrm{SnBr_4}$ being the transition from the ground level to this repulsive curve. Provided that the extrapolation of $D(\mathrm{SnBr_4})$ holds and that this repulsive curve is not too steep, the selective absorption should have a long-wave limit corresponding to the energy-difference

$$D_T = D(\mathrm{SnBr_4}) - D(\mathrm{SnBr_2}) = 105 \text{ kcal./mol.}$$

While in the case of $\mathrm{SnCl_4}$ only this one absorption can be observed in the quartz ultra-violet, in that of $\mathrm{SnBr_4}$ *two more* regions of selective absorption should be observable. The separation of the $^2\mathrm{P}$ term of Br mentioned above is 3685 cm.$^{-1}$ or about 10·5 kcal./mol., while for the Cl atom the same term-difference is 881 cm.$^{-1}$, which is too small to be observed in continuous absorption spectra. Above the level belonging to the system $\mathrm{SnBr_2} + 2\mathrm{Br}(^2\mathrm{P}_{3/2})$ two more levels will exist corresponding to $\mathrm{SnBr_2} + \mathrm{Br}(^2\mathrm{P}_{3/2}) + \mathrm{Br}(^2\mathrm{P}_{1/2})$ and to $\mathrm{SnBr_2} + 2\mathrm{Br}(^2\mathrm{P}_{1/2})$. The transition to the repulsive curves involving these levels of the separated system should therefore produce two more regions of selective absorption, the products of photodissociation being one excited and one unexcited Br atom in the second region and two excited Br atoms in the third region. Provided all three repulsive curves are rather flat and run more or less parallel to each other, the beginnings of absorption of the second and third regions will correspond to energies of $105 + 10{\cdot}5 = 115{\cdot}5$ and $105 + 21 = 126$ kcal./mol. respectively while the maxima will also show distances of the order of 3685 cm.$^{-1}$

Sharma(3) found one long-wave limit in the spectrum of $\mathrm{SnBr_4}$ at λ3510 but no structure. Introducing the substance directly into an absorption cell of length 1 cm. and heating it by means of a current of warm air, we have observed all three predicted regions of selective absorption at low vapour pressures. At a pressure at which the points of retransmission are just about to disappear the three long-wave limits are at $\lambda\lambda$3471, 2995 and 2442 or 83, 97·5 and 116 kcal./mol. For the first two absorption regions the maxima also could be determined at $\lambda\lambda$3063 and 2995, $\nu = 32638$ and 36646 their difference being 4000 cm.$^{-1}$ The difference of the limits is in 14·5 and 18·5 kcal./mol. The fact that the three beginnings of absorption show an absolute difference of about 15 kcal./mol. against the predicted ones is of no consequence. Not only has $D(\mathrm{SnBr_4})$ been extrapolated from $D(\mathrm{SnCl_4})$, but the heat of formation of $\mathrm{SnBr_2}$ is an old figure by Berthelot, and $S(\mathrm{SnBr_2})$ has been extrapolated, and both values together may easily be incorrect by 15 kcal./mol. Under these conditions, it is rather surprising that the experimental values approach the predicted ones at all. More important is the fact that the differences both between the three limits and also between the two maxima are all of the order of magnitude of the doublet separation of Br. Above all it is most significant that three different regions of absorption with this energy difference are observed. Since Br possesses only one excited term in this region, the second energy of excitation being 63,430 cm.$^{-1}$ or about 181 kcal./mol., this obviously establishes that two Br atoms are split off in this photolytic process. Without the second atom neither the doubling of the energy differences of the first two long-wave limits nor the very existence of a third region of selective absorption could be understood. Otherwise it would mean that the radical $\mathrm{SnBr_3}$ produces the third maximum just at the required wave-length, but since the same phenomenon is found again in, for example, $\mathrm{CHI_3}$ and $\mathrm{CI_4}$, $\mathrm{CHBr_3}$ and $\mathrm{CBr_4}$, such an interpretation is obviously impossible.

§4. ALKYL HALIDES; THERMOCHEMICAL CALCULATIONS

The absorption spectra of molecules of $\mathrm{Sn}X_4$ type lead to an interpretation of the photodissociation processes similar to that for molecules formed by atoms of the fifth and sixth groups in their state of maximal valency; and there is no reason why organic molecules should behave differently. Molecules $\mathrm{C}X_2$ are not stable compounds in the chemical sense; however, this is not an inherent property of organic molecules, but is mainly due to the large sublimation energy of carbon itself. While the formation of gaseous C and H atoms has to overcome the sublimation energy of carbon (~156·2 kcal./mol.) plus the dissociation energy of H_2 (102·7 kcal./mol.), even with the slightly higher value for the C—H bond in CH_2 deduced below, the formation of CH_2 from gaseous atoms liberates only 228 kcal./mol. Only if the same C atom, whose sublimation energy has been taken account of already, forms two more C—H bonds is an excess of energy liberated, since $D(\mathrm{CH_4}) = 379\cdot7$ kcal./mol., while $S(\mathrm{C}) + 2D(\mathrm{H_2}) = 361\cdot6$ kcal./mol. For the metallic elements of the fourth group the sublimation energies are lower and molecules of MX_2 type have therefore a greater probability to be stable in the chemical sense. This difference of behaviour is, however, of no importance whatever as to the relative positions of the energy levels of the system C + 4H, on which its photodissociation depends.

The atomic energies of dissociation of organic molecules necessary for comparison with the absorption spectra are obtained in the usual way. From the heat of combustion (*HC*) the heat of formation from the element (*Q*) is calculated, and from the latter *D* is derived by means of Born's cycle. Iodoform ($HC = 162\cdot1$) may serve as an example.* From the equation

$$[\mathrm{CHI_3}] + \tfrac{5}{4}(\mathrm{O_2}) = (\mathrm{CO_2}) + \tfrac{1}{2}\mathrm{H_2O} + \tfrac{3}{2}[\mathrm{I_2}] + 162\cdot1,$$

it follows that

$$[\mathrm{C}] + \tfrac{1}{2}(\mathrm{H_2}) + \tfrac{3}{2}[\mathrm{I_2}] = [\mathrm{CHI_3}] - 33\cdot6$$

and

$$(\mathrm{C}) + (\mathrm{H}) + 3(\mathrm{I}) = [\mathrm{CHI_3}] + 249\cdot4$$

or

$$D \text{ of gaseous } (\mathrm{CHI_3}) = 241 \text{ kcal./mol.}$$

The values in kcal./mol. used in these calculations are as follows:

$$2(\mathrm{H}) - (\mathrm{H_2}) = 102\cdot72,$$
$$2(\mathrm{O}) - (\mathrm{O_2}) = 116\cdot40,$$
$$(\mathrm{C}) - [\mathrm{C}] = 156\cdot2,$$
$$2(\mathrm{Cl}) - (\mathrm{Cl_2}) = 56\cdot9,$$
$$2(\mathrm{Br}) - (\mathrm{Br_2}) = 45\cdot23,$$
$$(\mathrm{Br_2}) - \mathrm{Br_{2(liq)}} = 7\cdot69,$$
$$2(\mathrm{I}) - (\mathrm{I_2}) = 35\cdot39,$$
$$(\mathrm{I_2}) - [\mathrm{I_2}] = 14\cdot88,$$
$$[\mathrm{C}] + (\mathrm{O_2}) = (\mathrm{CO_2}) + 94\cdot27,$$
$$\tfrac{1}{2}(\mathrm{H_2}) + \tfrac{1}{2}(\mathrm{Cl_2}) = (\mathrm{HCl}) + 21\cdot9,$$
$$(\mathrm{HCl}) - \mathrm{HCl_{aq.}} = 8\cdot4,$$
$$(\mathrm{H_2}) + \tfrac{1}{2}(\mathrm{O_2}) = \mathrm{H_2O_{liq.}} + 68\cdot31.$$

The value 156·2 for the heat of sublimation of carbon is in agreement with the general trend of thermochemical literature, which inclines more and more to a value slightly higher than 150. It is calculated* from $D(CO) = 10{\cdot}45$ V., which as discussed earlier[5, 6] to our mind is still the best available value. If, however, the value 150 kcal./mol. is preferred, all energies of dissociations have to be reduced by 6·2. This would decrease the final D_T values by 2–3 kcal./mol. The results of these calculations are collected in table 2. For CH_2I_2, CHI_3, and $CHBr_3$ the heats of sublimations are not known. The calculation from Forcrand's rule gives slightly too high values for these organic compounds as can be seen by calculating some of the known energies of sublimation in this way. Therefore 2, 8, and 10 kcal./mol. respectively have been finally adopted for these three compounds, the possible error is in any case negligible. It is generally assumed that the products of combustion of halides are $HCl_{aq.}$, $Br_{2\,liq.}$ and $[I_2]_{solid}$, and the values for Q are calculated according to this view. It may be due to an error of measurement or to a different reaction, that some of the values obtained for D obviously are not correct, as can be seen from the differences of the D values in the last column. The replacement of one H atom by a Cl atom decreases the energy of formation by 21–26 kcal./mol., if the values of CH_4, CH_3Cl, $CHCl_3$ and CCl_4 are taken into account. Calculation for CH_2Cl_2 gives 347 with a difference of 12 against $D(CH_3Cl)$ and of 33 against $D(CHCl_3)$, the mean of these two differences being 22·5. Hence the true value of $D(CH_2Cl_2)$ will be about 335 kcal./mol. Again $D(CH_4) - D(CH_3Br)$ indicates a decrease of 35 for the replacement of H by Br, but $D(CHBr_3)$ indicates 25 or 15 when compared with CH_4 or CH_3Br respectively. This value will therefore be too high; and since Thomsen's results have often been shown to be quite reliable, we adopt 30 as the weighted mean for this difference, and $D(CH_4) - 90 = 290$ kcal./mol. as the true energy of formation of $CHBr_3$. In the same way $D(CBr_4)$, for which no thermochemical data are available, is estimated as about 260 kcal./mol. $D(CI_4)$, for which again no thermochemical data are available, is placed at ~176, four times the difference $D(CH_4) - D(CH_3I)$ being deducted from $D(CH_4)$.

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* All values are taken from Landolt-Boernstein tables. Some of the figures are slightly different from those used in previous publications⁽¹⁾. In particular $S(\mathrm{I_2})$ has been changed from about 3 to 7·4 kcal./g. atom on account of Kelley's critical review of all available data. All other changes are small.

Table 2

	HC	*Q*	*D*	Differences of *D*
1. CH_4	212·79 (R.)	18·1	379·7	
2. CH_3Cl	176·95 (T.)	19·8	358·5	(1–2) : 21·2
3. CH_2Cl_2	106·8 (B.)	31·3	347 (335)	(2–3) : 12
4. $CHCl_3$	107·03 (T.)	21·4	314·4	(3–4) : 33; (2–4) : 44 = 2 × 22; (1–4) : 66 = 3 × 22
5. CCl_4	75·93 (T.)	18·34	288·3	(4–5) : 26; (1–5) : 92 = 4 × 23
6. CH_3Br	184·71 (T.)	8·2	345	(1–6) : 35
7. $CHBr_3$	90·3 (P.S.)	38·2	315 (290)	(6–7) : 30 = 2 × 15
8. CBr_4	—	—	(~260)	
9. CH_3I	196·08 (T.)	−6·8	328·6	(1–9) : 51·1
10. CH_2I_2	178·4 (B.)	−69·2	283 (?)	(9–10) : 46
11. CHI_3	162·1 (B.)	−33·6	223	(10–11) : 61; (9–11) : 106 = 2 × 53
12. CI_4	—	—	(~176)	

(R.) = Rossini; (T.) = Thomsen; (B.) = Berthelot; (P.S.) = Popoff and Schirokich. For references see Landolt-Boernstein tables.

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* With 5·05 instead of 5·09 V. as in the original paper for $D(O_2)$, according to H. P. Knauss and S. S. Ballard, *Phys. Rev.* **48**, 796 (1935).

To interpret the absorption spectra of the alkyl halides CX_4, CHX_3, CH_2X_2, and CH_3X in a similar manner as those of $SnCl_4$ and $SnBr_4$, the dissociation energies of the molecules CH_2, CHX, and CX_2, should be known, or in other words the bond energies $C^{II}—H$ and $C^{II}—X$ in saturated molecules formed by unexcited divalent C atoms. At present there is no other way but to extrapolate these energies according to the known ratio

$$D(SnCl_4) : D(SnCl_2) = 5 : 3 \sim D(CX_4) : D(CX_2).$$

In other words it is assumed, that the excited electronic levels of a system $C+4X$ have a similar position compared with the known ground level of the system as those of $Sn+4Cl$ against the ground state of unexcited $SnCl_4$. Such an extrapolation cannot be expected to give more than approximate values but as a matter of fact it will be seen that the agreement of the estimated figures with those measured experimentally is much better than was hoped for originally. This extrapolation therefore falls in line with the many empirical laws and rules, known in atomic physics, which, beginning with atomic terms up to the constants of diatomic molecules like ω, r, or D, represent quite well the change of such a constant in a homologous series of related atoms or molecules.

For CH_4 the position of the energy levels is as follows: $D(CH_4)$ being 379·7 kcal./mol., 228 is obtained for $D(CH_2)$ according to the above ratio, and this gives 114 for the mean bond energy $D_B(C^{II}—H)$. According to the theory of Heitler and London, the C atom becomes tetravalent on excitation from s^2p^2 to sp^3 or p^4. While Heitler and Herzberg$^{(7)}$ assumed that the lowest possible term of tetravalent carbon, i.e. $sp^3\ {}^5S$ has an energy of excitation of 1·6 e.V. only, Lessheim and Samuel$^{(5)}$ pointed out that this energy is much higher and estimated 5·2 V. for $sp^3\ {}^5S$ and 17·4 V. for $p^4\ {}^3P$ from the spectrum of C^+. Simultaneously Van Vleck$^{(8)}$ estimated 5–8 V. for the excitation energy of ^5S and later reduced this value to 4·3 V. on account of new measurements of Edlén for N^+ and O^{++} and a new extrapolation by Bacher and Goudsmit. At the same time he concludes from wave-mechanical calculations, that the term belonging to the configuration sp^3 in which C becomes tetravalent is not the term ^5S but a higher one at about 7 V. (161 kcal./mol.) on account of a strong repulsive force between the H atoms. If this be true the adiabatic dissociation energy of CH_4 is $370+161=532$ kcal./mol. and the mean bond energy $D_B(C^{IV}—H)=532/4=133$ kcal./mol. With an excitation energy of about 100 kcal./mol. for ^5S, $D_B(C^{IV}—H)$ comes to 120 kcal./mol. Bond energies involving activated s^2 groups are naturally stronger than those involving the p electrons only, as can be seen from the example of CO_2, where the energy of adiabatic dissociation has been calculated$^{(5)}$. Thus both figures show that the value 114 kcal./mol. for $D_B(C^{II}—H)$ is by no means too high. In the radical CH_3 the bond energy will be strengthened on account of decreased repulsion of the H atoms, but weakened by the disturbing electron not taking part in the linkage. The latter influence will probably be the stronger one and therefore the C—H bond will be weaker in CH_3, and stronger in CH_4, than that indicated by the mean ratio calculated above, and the same is true for CH_2 and CH. (The dissociation energy of CH cannot be extrapolated directly from the band spectrum, the anharmonic constant not being known.) The corresponding values for $D(CX_2)$ can be estimated in the same approximate manner to be 172, 156 and 104 kcal./mol. for $X=$ Cl, Br and I respectively. The mean bond energies $D_B(\mathrm{C^{II}}—X)$ are in the same order 86, 78, and 53 kcal./mol. With C(^{5}S) the bond energies $D_B(\mathrm{C^{IV}}—\mathrm{X})$ of the molecules formed by tetravalent carbon will be about 97, 90 and 69 kcal./mol. for $X=$ Cl, Br and I respectively.

§ 5. ABSORPTION SPECTRA OF METHYL HALIDES

The first experimental confirmation of the value 222 kcal./mol. for $D(\mathrm{CH_2})$ will be found in the absorption spectra of the methyl halides. The absorption spectra of the monohalides of this series have been measured by Herzberg and Scheibe(9), and their results have been confirmed by later work(10, 4). The beginning of absorption (taken at a value of the absorption coefficient of about 1/10 of the selective maximum and about equal to the value of the following point of retransmission) lies at a wave-length corresponding to 151, 123, and 102 kcal./mol. for $\mathrm{CH_3Cl}$, $\mathrm{CH_3Br}$, and $\mathrm{CH_3I}$ respectively. On the basis of 92 (or with more recent values 95) kcal./mol., equal to one-quarter of $D(\mathrm{CH_4})$ for the C—H bond (i.e. if the excitation of the C atom for it to become tetravalent is not considered), the values of about 72, 59 and 45 kcal./mol. are conventionally deduced for the energies of the C—Cl, C—Br, and C—I bonds. But compared with these values the experimental long-wave limits are about 100 per cent too high and this discrepancy has never been properly understood. Even if one-quarter of the excitation energy of C(^{5}S), equal to 25 kcal./mol., are added to the above energies of the C-X bonds, the resulting values of 98, 84 and 70 kcal./mol. are still far too low in the light of the experimental results. The same is true, if the values deduced (as above) from those of $D(CX_4)$ are taken into account; these are 97, 90 and 69 kcal./mol. To account for these high experimental values a high excitation of the dissociation products has been assumed and in addition an extremely steep repulsive curve (whose tangent above the minimum of the unexcited state would form an angle of about 45° with the internuclear axis). Both these assumptions are theoretically possible, but do not in the least agree with our experience as to the photodissociation of other multiatomic covalent molecules.

If, however, the unexcited C atom is divalent only the photodissociation will take place, as in $\mathrm{SnCl_4}$, by a transition from the ground level of the molecule $\mathrm{CH_3}X$ to the repulsive level of the system $\mathrm{CH_2}+\mathrm{H}+X$. The position of this level is $D_T=D(\mathrm{CH_3}X)-D(\mathrm{CH_2})$, and for $\mathrm{CH_3Cl}$, $\mathrm{CH_3Br}$, and $\mathrm{CH_3I}$ the values 131, 117 and 103 kcal./mol. are obtained deducting 228 from the atomic heat of formation. In table 3 these figures are compared with those of Herzberg and Scheibe, Henrici, and Hukumoto. Hukumoto's values are slightly too low, because, as he states, only the values for the highest pressures are recorded in his paper. Considering the many unavoidable extrapolations and the experimental difficulty of determining the long-wave limit of the vibrationless molecule, it may be said that the gross discrepancy, discussed above, has entirely disappeared and that the new interpretation submitted here is fully supported by experimental evidence.

Table 3

Molecule CH_3X	Dissociation products	$D_T = D(CH_3X) - D(CH_2)$ (kcal./mol.)	Observed long-wave limit (kcal./mol.)		
			Herzberg and Scheibe	Henrici	Hukumoto
CH_3Cl	$CH_2 + H + Cl$	131	151	143	125
CH_3Br	$CH_2 + H + Br$	117	123	117	96
CH_3I	$CH_2 + H + I$	103	102	96	90*
$CH_3.OH$	$CH_2 + H + OH$	140	142	—	—

* In the original paper 70·2 is given for CH_3I, an obvious misprint, since the recorded wave-length $\lambda 3100 = 90{\cdot}2$ kcal./mol.

Since the photodissociation involves the separation of one halogen atom, a second maximum of selective absorption should be expected for CH_3Br and CH_3I at a wave-length representing a value 10·5 and 21·5 kcal./mol. higher, respectively, in accordance with the excitation energy of the Br and I atoms. For CH_3I this maximum has been found by Hukumoto using a thin film of liquid methyl iodide as absorbing layer, with an energy difference of 0·75 e.V. from the first maximum, while the doublet separation of I is $7600 \text{ cm.}^{-1} = 0{\cdot}94 \text{ e.V.} = 21{\cdot}5$ kcal./mol.

Herzberg and Scheibe have also measured the absorption of methyl alcohol and find a condition similar to those of the halides. The beginning of absorption lies at about $\nu 50000 = 142$ kcal./mol. From the heat of combustion (182·58 kcal./mol.), it follows that $Q = 48{\cdot}3$ and D (for gaseous $CH_3.OH$) $= 468{\cdot}1$, and when $D(CH_2)$ is deducted, a value 240 kcal./mol. is obtained. On account of the general similarity of the absorption curve with that of the methyl halides Herzberg and Scheibe assume that the dissociation involves an OH radical. The bond energy of this radical is independently known(11) to be 100 kcal./mol. Deducting this figure we obtain 140 kcal./mol. for the dissociation $CH_3.OH \rightarrow CH_2 + H + OH$, again in good agreement with the experimental result.

§ 6. ABSORPTION SPECTRA OF HIGHER ALKYL IODIDES

The iodides are easily the most interesting compounds, because, on account of their smaller bond energies, a greater part of the absorption spectrum lies in the quartz ultra-violet. We shall deal with them first (table 4).

For carbon tetraiodide it follows from the figures of table 2 that

$$D(CI_4) - D(CI_2) = 176 - 106 = 70 \text{ kcal./mol.}$$

The first region of absorption should therefore have a long-wave limit of this value and should correspond to the dissociation process $CI_4 \rightarrow CI_2 + 2I(^2P_{3/2})$. At distances corresponding to 21·5 kcal./mol., two more regions of absorption should follow towards shorter waves, corresponding to the dissociations

$$CI_4 \rightarrow CI_2 + I(^2P_{\frac{3}{2}}) + I(^2P_{\frac{1}{2}}) \quad \text{and} \quad CI_4 \rightarrow CI_2 + 2I(^2P_{\frac{1}{2}}).$$

Table 4

Molecule	Dissociation products	D_T calculated (kcal./mol.)	Observed beginnings of absorption	
			(kcal./mol.)	λ (A.)
CI_4	CI_2+2I	70	72	3930
	CI_2+I+I^*	91·5	89·5	3177
	CI_2+2I^*	113	102	2795
CHI_3	$CHI+2I$	56	67	3780
	$CHI+I+I^*$	77·5	88	3229
	$CHI+2I^*$	99	99	2872
CH_2I_2	CH_2+2I	55	81	3499
	CH_2+I+I^*	76·5	107	2640
	CH_2+2I^*	98	120	2365
CBr_4	CBr_2+2Br	104	97	2932
	$CBr_2+Br+Br^*$	114·5	116	2453
	CBr_2+2Br^*	125	—	—
$CHBr_3$	$CHBr+2Br$	98	103	2750
	$CHBr+Br+Br^*$	108·5	114	2497
	$CHBr+2Br^*$	119	129	2195 (?)

The long-wave limits of these absorption regions therefore should lie at wave-lengths corresponding to about 91·5 and 113 kcal./mol., the maxima having a separation of approximately 7600 cm^{-1}.

The absorption spectrum of carbon tetraiodide has not previously been investigated. We observed it by introducing the substance directly into the absorption tube and heating it with a current of warm air up to about 60° C. (cf. figure 1). All the predicted maxima have been observed (cf. table 1). We obtained also the two first maxima at 345 and 305 mμ. in a solution of CI_4 in CCl_4, the third one being overlapped by the self absorption of the solvent. Since iodine has no absorption at these wave-lengths, this observation shows that the substances did not appreciably decompose on heating, even though some of the bands of I_2 at shorter waves could faintly be seen on the plates. The differences of the maxima, 4227 and 4813 cm^{-1} are slightly less than the expected ones, probably on account of the repulsive curves not running entirely parallel. The long-wave limits at λλ3930, 3177 and 2795 A. correspond to 72, 89·5 and 102 kcal./mol., and comparison with the predicted values, 70, 91·5 and 113, leaves little doubt that the above interpretation is essentially correct.

The absorption of iodoform was first measured by Scheibe and collaborators⁽¹²⁾ in various solvents; e.g. in hexane it shows maxima at λλ348, 307 and 275 mμ. Although the distance in cm^{-1} between these maxima is about 4800 and 3800 respectively, i.e. again slightly smaller than what could be expected from the excitation energy of iodine, this can easily be accounted for, as in the case of CI_4, by the repulsive curves approaching each other; and, as a matter of fact, the existence of the third maximum appeared to be so significant, that it first led us to undertake the present investigation. Henrici$^{(10)}$ was unable to measure the absorption of iodoform since in his apparatus it was not possible to produce sufficient vapour pressure. Our measurements have been carried out similarly to those of CI_4. All those maxima have been observed for the vapour state, figure 2, the wave-length of the maxima and long-wave limits being listed in tables 1 and 4. Deducting from $D(CHI_3) = 223$ the values $D_B(C^{II}—H) = 114$ and $D_B(C^{II}—I) = 53$, we obtain a value of D_T equal to 56 kcal./mol. Provided the repulsive curves run flat and parallel, three regions of absorption are expected with long-wave limits corresponding to 56, 77·5 and 99 kcal./mol. The wave-lengths observed experimentally correspond to 67, 88 and 99 kcal./mol. Although the differences between the maxima again are slightly smaller than the separation of the ^2P term of I, the existence of these absorption regions with long-wave limits so close to the estimated positions makes it practically certain that the decomposition has taken place according to the equation: $CHI_3 + h\nu = CHI + 2I$. The possibility of a process like $CHI_3 \rightarrow CI_2 + H + I$ would lead to a long-wave limit corresponding to 117 kcal./mol., equivalent to $D(CHI_3) - D(CI_2)$, and since only one I atom is split off, only two maxima would exist. Such a long-wave limit is impossible for a coloured compound.

The spectrum of methylene iodide has been investigated previously by Iredale$^{(13)}$, Henrici$^{(10)}$ and Hukumoto$^{(4)}$. Iredale and Henrici record only one maximum in the quartz ultra-violet, at about λ3000, and Henrici also observes two small regions of selective absorption at λλ1865 and 1970, which being very close together and situated directly at the beginning of the region of band absorption are probably diffuse bands. Hukumoto records three maxima at λλ2860, 2460 and 2210. Our own experimental results agree with those of Hukumoto. For some time we were unable to obtain all three maxima in the vapour state. We therefore measured quantitatively the absorption curve of CH_2I_2 dissolved in ether. The sample used for this purpose was carefully purified, free iodine being removed by washing it with a weak solution of sodium hyposulphite and drying it after separation by means of calcium chloride. The absorption curve shows all three maxima very clearly, but the absorption coefficient of the middle one is lower than of both its neighbours. The absorption coefficients* of the three maxima, counted from longer to shorter waves are $\log K = 3{\cdot}5$, $2{\cdot}8$ and $3{\cdot}3$ respectively. In the vapour state, the middle maximum is easily overlapped by the others and can be obtained only by careful adjustment of the vapour pressure, the probability of transition being considerably smaller for it than for the others. The three beginnings of absorption are at λλ3499, 2640 and 2365, or 81, 107 and 120 kcal./mol. respectively, the maxima at νν34062, 40638 and 45031, with differences of 6576 and 4393 cm.$^{-1}$ There are various possibilities for the process of dissociation of the molecule CH_2I_2. Its dissociation products may be $CI_2 + 2H$, $CHI + H + I$, or $CH_2 + 2I$. Deducting $D(CI_2)$ from $D(CH_2I_2)$, we obtain 177 kcal./mol. for the first process, and no maxima due to excited

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* K represents Bunsen and Roscoe's extinction coefficient defined usually by $I = I_0 \times 10^{-kcd}$.

I atoms are possible. In the second case the energy difference

$$D(CH_2I_2) - D_B(C^{II}—H) - D_B(C^{II}—I)$$

gives a long-wave limit of 116 kcal./mol., and one further region of absorption beginning at 137·5 kcal./mol. is expected. The third possibility indicates a long-wave limit at $D(CH_2I_2) - D(CH_2)$, equal to 55 kcal./mol., and two more maxima with beginnings at 76·5 and 98 kcal./mol. Actually the experimental values do not agree with any of these calculated thermochemically. This may be due partially to the heat of combustion being an older value of Berthelot's, but the discrepancy is more than can probably be accounted for in this way. On the other hand, the very good agreement obtained with other molecules of this kind shows the present view to be essentially correct, and the existence of three maxima indicates the last of the three possible dissociation processes, in which two I atoms are separated simultaneously. It therefore appears as if the repulsive curves, and particularly the lower two of them, have a rather steep slope which increases the energy difference from the ground level at that internuclear distance where the transition occurs.

§ 7. ABSORPTION SPECTRA OF HIGHER ALKYL BROMIDES

The value 260 kcal./mol. of $D(CBr_4)$ has been estimated, no thermochemical measurement being available. From this $D_B(C^{II}—Br) = 78$ has been obtained, which leaves 104 kcal./mol. for $D_T(CBr_4)$. According to the photolytic process $CBr_4 \rightarrow CBr_2 + 2Br$, $CBr_4 \rightarrow CBr_2 + Br + Br^*$ and $CBr_4 \rightarrow CBr_2 + 2Br^*$, three regions of selective absorption with beginnings at 104, 114·5 and 125 kcal./mol. are expected. Carbon tetrabromide is one of the less stable molecules of this series, and decomposes easily when heated to obtain the required vapour pressure. Henrici(10) therefore found only one long-wave limit, corresponding to about 81 kcal./mol. We have been able to determine two regions of selective absorption with long-wave limits at λλ2932 and 2453 (97 and 116 kcal./mol.) and a maximum at λ2525 without succeeding in tracing the second maximum or a further region of absorption. The energy-difference between the long-wave limits agrees almost exactly with the excitation energy of the Br atom, and considering the inaccuracy of the estimated value of $D(CBr_4)$ the agreement between the calculated values 104 and 114·5 and the observed values 97 and 116 kcal./mol. is very good indeed.

For $CHBr_3$ again three regions of absorption are expected. Deducting from $D(CHBr_3) = 290$ the values $D_B(C^{II}—H) = 114$ and $D_B(C^{II}—Br) = 78$, a value 98 kcal./mol. is obtained for the process $CHBr_3 \rightarrow CHBr + 2Br$. The long-wave limits of the two regions corresponding to one or two excited Br atoms as dissociation products would then correspond to 108·5 and 119 kcal./mol. These figures, however, may be incorrect by some kcal./mol. on account of the discrepancy in $HC(CHBr_3)$, discussed above.

While Hukumoto(11) records a long-wave limit at λ2690 only, Henrici(10) finds λ2863 and a maximum at a very large distance away at λ1695. We have found two regions of selective absorption and the beginning of a third one. For the long-wave limits we obtain λλ2750, 2497 and 2195, corresponding to 103, 114 and

129·5 kcal./mol., both differences being about 11 kcal./mol. in very good agreement with the bromine excitation of 10·5 kcal./mol. The two maxima have $\lambda\lambda$2559 and 2275, $\nu\nu$39066 and 43942 the difference of 4876 cm.$^{-1}$ is again in fair agreement with the term difference of Br. It can however be seen from figure 3, that the second maximum and the third limit occurring in a region in which the density of the spectrum is already weak, are difficult to locate and therefore less accurate. The above values are means from three spectrograms. All three values of the beginnings agree closely with the predicted ones.

§ 8. HIGHER ALKYL CHLORIDES

The absorption spectra of the higher chlorides exhibit maxima only in the Schumann region, and the maxima due to the excitation energy of one or two Cl($^2P_{\frac{1}{2}}$) atoms cannot be distinguished from the first maximum, this excitation energy being too small. Without accurate knowledge of the position of the maximum and its absorption coefficient, the determination of the long-wave limit of the vibrationless molecule in the quartz ultra-violet therefore becomes rather inaccurate and the discrepancies between the results of various authors is considerably increased. The energies of dissociation and the value of D_B(C$^{\mathrm{II}}$—Cl) have been calculated above; and in table 5 we compare the values of the beginning of the absorption with the D_T values.

Table 5

	Dissociation products	$D(CX_4) - D(CX_2) = D_T$ (kcal./mol.)	Long-wave limit (kcal./mol.)		
			Henrici	Hukumoto	Present paper
CCl_4	$CCl_2 + 2Cl$	$288 - 172 = 116$	124	117	~121
$CHCl_3$	$CHCl + 2Cl$	$314 - 186 = 128$	134	121	~128
CH_2Cl_2	$CHCl + H + Cl$ (?)	$335 - 186 = 149$	136	123	—

Considering the experimental difficulties the agreement is again quite good.

§ 9. DISCUSSION OF RESULTS

It has been seen that the absorption spectra of molecules of MX_4 type are in good agreement with the interpretation of the photolytic process discussed above. According to this view one of the dissociation products is a saturated molecule $MX_2(^1\Sigma)$ and the absorption of light induces an excitation of the molecule MX_4 from its ground level to the repulsive curve $MX_2(^1\Sigma) + 2X$. The significance of this type of photolytic dissociation is that it does not refer to any bond energy. The possibility of the breaking up of a molecule in this way has been recognized previously; Mecke(14) particularly has discussed it at greater length. A mechanism of photodissociation rather nearly related to this conception has been set up for keten by Norrish(15); and certain results of Terenin(16), which will be discussed below, also support this type of interpretation. Some years ago, on the basis of the meagre experimental results then available, one of us suggested(17) a division of the photodissociation processes of inorganic molecules, according to the two types involving bond energies and radicals or excitation to the repulsive curve produced by saturated molecules of lesser state of valency. This has been justified by many subsequent experimental results(18). This conception which, in fact, involves the rupture of two bonds by an amount of energy less than the bond energy of one of them, is therefore not as extraordinary as it appears at first.

Attention may therefore be directed to the experimental results of Terenin(16) and of Norrish(15) and their collaborators, which strongly support the interpretation presented here. Terenin illuminated SnI_4 vapour of low pressure with ultra-violet light of short wave-length and obtained a bright visible fluorescence of the band spectrum of I_2. From our results on $SnBr_4$ we are now able easily to understand his result. The upper level for the visible I_2 bands is known to dissociate into one excited and one unexcited atom, and the recombination of two such atoms produces an I_2 molecule in this excited electronic level. Illumination with any light of shorter wave-length than the second long-wave limit will result in a decomposition $SnI_4 \rightarrow SnI_2 + I + I^*$ and the recombination of the two atoms produces the band spectrum of I_2 in emission. Terenin's experiments show that, at least for SnI_4, such a recombination occurs frequently and immediately after the decomposition of the original molecule, since the life-time of the two free atoms is increased on account of the low pressure.

The experiments of Norrish and his collaborators concern the photodissociation of ketones. While in heavier ketones the hydrocarbon chain is ruptured by the action of light, simple ketones decompose into hydrocarbon and carbon monoxide. Formaldehyde may be taken as an example. It possesses a band spectrum whose origin, according to the vibrational analysis, lies at slightly longer waves than $\lambda 3530$, equal to 80 kcal./mol. A point of predissociation is observed at $\lambda 2750$, equal to 103 kcal./mol., but, according to new conceptions for polyatomic molecules, decomposition by light will occur at appreciably longer waves than the point of predissociation, and the quenching of fluorescence should be taken as the true threshold value of photodecomposition(15). This happens near $\lambda 3600$, equal to 78 kcal./mol. The photochemical experiment shows indeed that photodecomposition begins at least at about $\lambda 3300$, equal to 86 kcal./mol., and the final products are formed according to the process $H_2CO \rightarrow H_2 + CO$. From comparison with other ketones and aldehydes it is obvious that the band spectrum belongs to the chromophoric group $>CO$, while the absorbed energy is transferred to other parts of the molecule by the coupled modes of vibrations. Since the energy of two C^{IV}—H bonds is at least twice 120, equal to 240 kcal./mol. (with C^3 sp^2 ^5S), and the contribution of two such bonds to the atomic energy of formation is $2 \times 95 = 190$ kcal./mol., Norrish assumes that the mechanism of photodissociation involves two steps, i.e.

$$H_2CO + h\nu = H + HCO,$$
$$HCO \rightarrow \quad H + CO(x^1\Sigma).$$

The primary change concerns the splitting of the true bond energy $D_B(C^{IV}—H)$ by the action of light, while the spontaneous decomposition of the remaining radical is due to the excitation energy liberated by the CO molecule on its transition from the excited (carbonyl) term, in which it possesses two free valencies, to the ground state $x^1\Sigma$ formed by O and divalent C (energy of reorganization).

This mechanism is very near to the view presented here, since it makes use of the repulsive curve originating in the level of $CO(x^1\Sigma)$, but, according to the results obtained for the CX_4 molecules, it appears as if it may be further simplified. We submit that the true bond energy* $D_B(C^{IV}—H)$ does not play any role in the photolytic process, but that photodissociation occurs simply by the excitation of the molecule H_2CO to the first repulsive curve, which is the level $2H + CO(x^1\Sigma)$. $Q(H_2CO)$ being 28·5, we obtain by means of Born's cycle $D(H_2CO) = 345·6$, and deducting $D(CO) = 241·1$, we obtain the level $2H + CO(x^1\Sigma)$ 104·5 kcal./mol.† above the ground level of H_2CO. The other possible repulsive level, $O + CH_2$, which includes the energy of reorganization of the CH_2 molecule, lies 14 kcal./mol. higher, since $D(H_2CO) - D(CH_2) = 118$ kcal./mol., and thereby explains why the decomposition by light liberates CO and not CH_2, whereas the electronic excitation of the band spectrum almost certainly concerns an electron of the carbonyl group. While the value of $D_B(C^{IV}—H)$ no longer agrees with the point of predissociation at 103 kcal./mol., the close agreement of this value with the above 104·5 kcal./mol. is obvious. It is true that the photodissociation begins at longer waves in the region of discrete band absorption, but this discrepancy occurs in both interpretations and even if not $D_B(C^{IV}—H)$ but $Q(C—H) = 1/4 . 380 = 95$ kcal./mol. could be considered as an explanation. The very existence of a discrete band spectrum suggests that in this region decomposition is due to transition from excited vibrational levels to the same repulsive curve, the more so since a single CO or CH vibration represents the considerable energy of 5 or 8·5 kcal./mol. respectively. The quantum yield in this region, which varies for different molecules of this type, will then depend on the percentage of the bands which, under the particular experimental conditions, are due to excited vibrational levels. The question as to the lowest repulsive curve in more complicated aldehydes and ketones cannot be answered at the present moment, and, moreover, the same view may not be applicable to processes of thermal decomposition. But it appears as if, at least for molecules with short hydrocarbon chains, this view of the simultaneous splitting of two bonds meets best the requirements of the results of photochemical experiments as to the main process of decomposition. Naturally such experiments always include the possibility of secondary reactions which may obscure the issue.‡ It is, however, significant that for keten $H_2C{=}CO$, where on account of the double bond there is no other alternative but to assume that both are fissured simultaneously, the mechanism set up by Norrish (on the basis of the new figures for the excitation of C) practically comes to the same result as that presented here.

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* The value of 103 kcal./mol. for $D_B(C^{IV}—H)$ used in the earlier papers of Norrish and collaborators is based on the estimate of 1·7 e.V. for $C(^5S)$ and is therefore much too low. The true values are discussed above in the thermochemical section of this paper.

† This value is, of course, independent of the exact absolute value of $D(CO)$, since $S(C)$ is derived from the latter, and is used again for $D(H_2CO)$.

‡ According to Spence and Wild(19) the mechanism of photodecomposition of acetone varies with temperature. This may be due to experimental conditions, which are not described in their preliminary note, or to the fact that the repulsive curve of the system $R + RCO$ is slightly lower than that of $2R + CO(^1\Sigma)$. For $D_B(C^{IV}—C)$ a value of about 115 kcal./mol. only can be deduced from the heat of sublimation of carbon and its energy of excitation to the term ^5S. The curve $2R + CO(^1\Sigma)$ will then be reached from excited vibrational levels of the ground term whose population increases with temperature.

These few remarks do not aim at an exhaustive explanation of the photodissociation of ketones, but they show that the conception of the excited repulsive terms of organic molecules provide an alternative interpretation in many cases. In spite of the fact that they represent a simultaneous rupture of those two bonds which are due to the original *s* electrons of C, N, S, etc., they have a lower position because they involve unexcited radicals without free valencies, and therefore often provide a very simple explanation of the decomposition of the molecule. To our mind their existence is established by the third maximum of the compounds of MX_4 type. On the application of this conception to more complex organic molecules we hope to report shortly.

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THE EFFECT OF PRESSURE AND TEMPERATURE ON THE OCCLUSION OF HYDROGEN BY PALLADIUM

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Received 9 *April* 1937. *Read in title* 11 *June* 1937

ABSTRACT. The X-ray method has been employed to investigate the occlusion of hydrogen by palladium when the pressure of the hydrogen surrounding the palladium and the temperature of the palladium are varied. Measurements were made of the parameter of palladium at temperatures of 80, 100, 120, 140 and 160° C. when the palladium was surrounded by an atmosphere of hydrogen, the pressure of which ranged from zero to 76 cm. of mercury. When the temperature was kept constant, a linear relation was found to exist between the lattice parameter and the pressure for both of the two phases in the system. For dilute solutions of hydrogen in palladium over the ranges of temperature and pressure investigated, the change in parameter of palladium due to the occlusion of hydrogen was found to vary directly as the pressure of the hydrogen and inversely as the square of the temperature of the palladium. The entrance of hydrogen atoms into the palladium lattice loosens the bonds between the palladium atoms, thus allowing them to separate more readily under the action of heat. The value of the parameter of pure palladium free of gas was found to be $3{\cdot}8825_6 \pm 0{\cdot}0003$ A. at 20° C., and the mean coefficient of thermal expansion between 0 and 300° C. to be $12{\cdot}7 \times 10^{-6}$ per ° C.

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§ 1. INTRODUCTION

The interactions of gases with metals have been extensively studied. Of all the systems examined it is probably the hydrogen-palladium system that has had the most attention, but the results of different investigators who have examined the system by various methods are not all in agreement. A full account of the work done in this field up to 1925 is contained in a paper by Lambert and Gates(1), who themselves made an important contribution to our knowledge concerning the relationships existing between hydrogen and palladium. They found that the relation between the pressure of hydrogen surrounding the palladium at any temperature and the concentration of the gas in the palladium, depended upon whether the pressure of the gas was increased or decreased to its final value. The ascending isothermal differed in shape from the descending isothermal, thus exhibiting a cycle similar to a hysteresis loop. This effect will be considered in detail in a later paper.

The present paper is concerned with the relation which exists between the lattice parameter of charged palladium, the temperature of the specimen and the pressure of the hydrogen surrounding it, attention being paid to the method of charging the specimen in view of the results just mentioned. Unlike the investigation of Lambert and Gates, the present work was carried out by X-ray analysis.

Yamada(2) appears to have been the first to use the X-ray method to investigate the effect of the occlusion of hydrogen on the crystal structure of palladium. The investigation was carried out under limited conditions and it is doubtful whether the deductions made were justified, as they were based on too small a number of observations. It was concluded however that the system contained only solid solution of hydrogen in palladium and no compounds of the two elements.

McKeehan(3) discovered two crystal lattices, both being face-centred cubic, one having a parameter of 3·900 A. and the other a parameter between 4·000 and 4·039 A. depending upon the degree of saturation. Two structures were suggested which would at the same time satisfy the observed cubic structures and the formula Pd_2H proposed by earlier investigators, but unfortunately these structures could not be checked by intensity-measurements owing to the low atomic number of hydrogen.

Linde and Borelius(4) also found two face centred cubic lattices, the parameter value 3·978 A. being associated with the compound Pd_2H. The measurements were made under definite conditions of temperature and pressure in an air-tight enclosure with a spectrum camera which yielded results accurate to within ± 0·01 A. The variation in parameter with electrolytic charging was also investigated with a focusing camera and two phases found as before, the accuracy of the parameter determination being of the order of ± 0·002 A. Measurements of the change in specific resistance of palladium with charging also pointed to the existence of two phases.

Hanawalt(5), from his measurements, was led to suggest the existence of the compound Pd_2H, and observations made on the *L* absorption limit of charged palladium pointed to the same conclusion.

A considerable amount of work has been done in Greifswald and Stockholm(6) on the adsorption of palladium and its alloys; the results favour the existence of two solid solutions. Different types of cameras were employed including the Debye type of spectrum camera and the camera described by Sachs and Weerts(7). The accuracy of the parameter-determinations was about 1 in 4000 and the exposures were made in air at room-temperature. The specimens were charged electrolytically and the hydrogen-content estimated from the current-strength and time as described by Berry(8). Rosenhall(9), using a focusing camera, the limits of accuracy being ± 0·002 A., also charged the specimens electrolytically, but measured the concentration after each exposure at room-temperature by heating the specimen *in vacuo*.

A comprehensive examination of a series of alloys was made by Hägg(10) who found that solutions of boron, carbon, nitrogen or hydrogen with the transition elements, one of which was palladium, possess a typically metallic character in comparison with solutions of these metalloids with other elements. The metalloid atoms were found to enter the metal lattice interstitially forming simple structures when $(r_x/r_m) < 0{\cdot}59$ and complicated structures when $(r_x/r_m) > 0{\cdot}59$, where r_x is the radius of the metalloid atom and r_m that of the metal atom.

In some of the foregoing investigations the specimen was charged with hydrogen electrolytically; it was then removed from the bath and allowed to dry before the X-ray exposure was made. In others the specimen was charged from the gaseous phase in an electric furnace, and after being charged it was allowed to cool in the gaseous atmosphere before making an exposure at room-temperature. In both of these procedures an element of uncertainty arises as to what may happen in the specimen between its charging with hydrogen and its exposure to X-rays. The investigations of Rosenhall and of Linde and Borelius are free from these sources of uncertainty.

In the present work the procedure is similar to that adopted by Linde and Borelius. The specimen is charged from the gaseous phase and the X-ray exposure is made whilst the specimen is maintained at a definite temperature and the pressure of the gas is kept constant. An attempt is made also to increase the accuracy of measurement. The high accuracy obtainable with the focusing camera renders it most suitable for observing small changes in parameter and the spectrum camera supplies information concerning the change in structure.

For simplicity in making reference, the two phases mentioned above will be referred to as the α and β phases, the α being what may be termed the palladium-rich phase, and the β the hydrogen-rich phase.

§ 2. APPARATUS

Two cameras were used in the investigation, one a focusing camera and the other a spectrum camera, both of which were designed for high-temperature work and could be mounted in enclosures which could be evacuated. An accuracy of at least 1 in 10,000 could be obtained in the values of the parameters as deduced from measurements made on films taken with the focusing camera. A much higher accuracy than this was obtainable under certain conditions. A high order of accuracy may also be obtained with the spectrum camera by adopting the extrapolation method suggested by Bradley and Jay(11). In this investigation the spectrum camera was used mainly to obtain the structure but on occasions it was also employed to obtain accurate values of the parameters although normally the focusing camera was used for this purpose. The cameras were carefully calibrated, and they both yielded consistent results.

§ 3. TEMPERATURE-MEASUREMENT

The measurement of temperature differed with the two cameras. In the focusing camera a thermocouple was inserted into the face of the thick copper sheet on which the specimen was mounted. This thermocouple was calibrated by inserting it in different materials whose melting points were known.

In the spectrum camera a different procedure was adopted; in this case use was made of the thermal expansion of a pure metal like silver, the parameter of the silver at different temperatures being employed to deduce the temperature. For this purpose a curve was drawn connecting the current passing through the heater and the temperature of the furnace. The calibration had to be carried out both *in vacuo* and in hydrogen. (*a*) *In vacuo.* The temperature attained with a given current passing through the heating-coil depends to a large extent on the pressure of the gas. It is therefore essential when taking a calibration *in vacuo* to render the enclosure and its connexions perfectly free from air leaks. The heater was calibrated for the range from room temperature to 300° C. The results are given in table 1.

Table 1. Calibration of heater *in vacuo*. Silver powder.
Cobalt radiation

Current through heater (amp.)	Parameter of silver (A.)	Temperature °C.
$0{\cdot}20_0$	4·0799	50 ± 5
$0{\cdot}30_0$	4·0842	105 ± 5
$0{\cdot}40_0$	4·0890	154 ± 5
$0{\cdot}50_0$	4·0941	226 ± 5
$0{\cdot}60_0$	4·1011	308 ± 5

(*b*) *In hydrogen.* Measurements with the precision camera showed that within the temperature range 15–140° C. and a hydrogen pressure-range 0 to 76 cm. of mercury the lattice parameter of silver was not altered by the presence of hydrogen, within the limits of accuracy of measurement. The calibration of the heater could therefore be carried out in exactly the same manner in hydrogen as *in vacuo.*

Two films taken under identical conditions of pressure and current showed that the lattice parameter of silver was the same after heating for 1 hour and for 3 hours, thus indicating that the motion of the governor of the clockwork, which consisted of a rotating vane, and the water-cooling system had produced a uniform steady temperature in 1 hour. Subsequently films were taken after the specimen had been heated for 1 hour. The following measurements show how the calibration curve at 100° C. was determined.

Two films were taken and the currents were chosen to give temperatures near 100° C. For example a current of $0{\cdot}55_0$ amp. gave a temperature of 88° C. whilst $0{\cdot}60_0$ amp. gave 120° C. These two points were plotted and the current necessary to give a temperature of 100° C. was deduced by interpolation. In this case the necessary current was $0{\cdot}57_0$ amp. A film taken with this current gave a parameter of 4·0838 A., corresponding to a temperature of 99° C. Thus, within the accuracy of the temperature measurements, the interpolation is justified.

Films were taken at various pressures from 10 to 76 cm. of mercury and the current i_{100} necessary to give 100° C. found by interpolation. The results are given in table 2 and the graph of i_{100} against the pressure p is given in figure 1. The current corresponding to a pressure of 0 cm. of mercury was read off the calibration curve *in vacuo* already determined. It is seen from the curve in figure 1 that the current is approximately independent of the pressure over the range 10–76 cm. of mercury, a rapid increase occurring over the first 10 cm. of mercury pressure.

Table 2. Calibration of heater in hydrogen

Film number	Pressure cm. Hg.	Current (amp.)	Parameter of silver (A.)	Temperature (° C.)	i_{100} (amp.)
8	75·3	0·55$_0$ 1 hr.	4·0828	87	0·57$_0$
9	75·3	0·55$_0$ 3 hr.	4·0829	88	
15	75·3	0·60$_0$ 1 hr.	4·0854	120	
26	75·3	0·57$_0$,,	4·0838	99	
18	66·0	0·60$_0$,,	4·0855	121	0·56$_5$
22	66·0	0·53$_0$,,	4·0824	82	
24	50·0	0·57$_0$,,	4·0847	111	0·55$_8$
28	50·0	0·55$_5$,,	4·0836	97	
19	36·0	0·55$_5$,,	4·0845	109	0·53$_8$
23	36·0	0·51$_0$,,	4·0829	88	
25	20·0	0·48$_0$,,	4·0824	82	0·53$_5$
27	20·0	0·50$_0$,,	4·0829	88	
29	10·0	0·48$_0$,,	4·0828	87	0·51$_3$
32	10·0	0·52$_0$,,	4·0842	104	

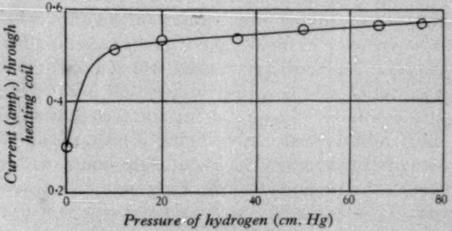

Figure 1.

§ 4. THE PREPARATION OF HYDROGEN

It is well known that impurities have a marked effect on the occlusive power of palladium for hydrogen. Maxted(12) found that a very small amount of sulphuretted hydrogen was sufficient to inhibit completely the adsorption of hydrogen. On exhausting at a temperature of 100° C. a volume of gas approximately equal to that of the sulphuretted hydrogen absorbed was evolved and was found on analysis to consist almost entirely of hydrogen, the sulphur being retained by the palladium.

The volume of the camera enclosure and the glass reservoir connected to it was of the order of 10 litres. It was therefore not expedient to generate the hydrogen by the electrolysis of barium hydroxide in the manner recommended for obtaining a very pure supply. Electrolysis of dilute acids or salts was not considered advisable, partly because of the slow rate of generation and partly because of the possibility of the formation of sulphur dioxide and sulphuretted hydrogen. It was finally decided to generate the gas in a Kipp apparatus by the action of pure hydrochloric acid on pure zinc, a few drops of a solution of cobalt sulphate being added as a catalyst to increase the velocity of reaction. The gas was bubbled slowly through the following train of purifying agents: (*a*) alkaline potassium permanganate; (*b*) a 5 to 10-per-cent solution of silver nitrate, to remove sulphuretted, arseniuretted and phosphoretted hydrogen, oxides of nitrogen, sulphur dioxide and halogens; (*c*) acid chromous chloride or alkaline pyrogallol, to remove traces of oxygen; (*d*) water to wash the gas free of traces of the other baths. The gas was then passed through calcium-chloride tubes and allowed to stand for some hours over phosphorus pentoxide contained in two large reservoirs, from which it could be passed through taps into either of the two camera enclosures. When measurements were made with a pressure of over 40 cm. of mercury it was necessary to close the taps connecting the enclosures with the glass reservoirs, as the latter were not of sufficient size to fill the whole apparatus to such pressures. A long boat containing phosphorus pentoxide and situated in the tube leading from the reservoirs served to remove the last traces of moisture from the gas. That the gas was rendered free from moisture is shown by the fact that the drying agent in this boat had to be renewed but once during the course of the work, which occupied about three years.

The presence of free sulphur in rubber was a possible source of sulphuretted hydrogen. As far as possible, rubber-glass connexions were not used in the generating apparatus, but for convenience in replacing purifying reagents (this was done about once every four weeks) it was necessary to make use of a few, the seals being made airtight with apiezon wax. Also, a rubber washer was used to render the camera enclosures airtight and ordinary pressure tubing was used in connecting parts of the apparatus. All these rubber parts before being connected up were boiled in a 10-per-cent solution of caustic potash for about eight hours, and then in water for three hours with frequent changing of water. They were then thoroughly dried in a current of warm air. This treatment was considered sufficient to remove any free sulphur from the rubber. Two small beakers containing caustic potash and phosphorus pentoxide were kept in the camera enclosures. The grease used for lubricating glass taps and rubber washers was made from sulphur-free rubber and pure petroleum jelly with a trace of paraffin wax. All parts of the apparatus were rendered gas-tight with apiezon wax.

The pressure in the apparatus was measured with a Bourdon gauge which was calibrated before and during the course of the work. A trap for oil vapour cooled to − 18° C. was inserted between the camera enclosure and the Cenco pump employed to evacuate the chamber.

§ 5. THE DEPENDENCE OF THE CONCENTRATION OF HYDROGEN IN THE SPECIMEN ON THE TEMPERATURE AND PRESSURE

In the X-ray study of alloy systems, it is necessary to know the composition of each alloy investigated. This entails little difficulty in metallic alloys, but in a metal-gas system difficulties arise owing to the number of factors which affect the composition. To determine the concentration of gas in the palladium specimens in this work would have needed an additional research, so that it was necessary to use the results obtained by other workers to translate the conditions of exposure into concentration when this was required. The concentration is usually expressed as the ratio of the number of atoms of hydrogen to the number of atoms of palladium and is denoted in symbolic form by H/Pd.

The most comprehensive set of {pressure, concentration} curves is that given by Hoitsema and Roozeboom(13), who used palladium in the form of powder and sponge. These curves were obtained with increasing pressure of hydrogen, which was the procedure mainly followed in this section of the present investigation. Also the curves cover a very wide range of temperature. In the absence of other data these curves were adopted for estimating the concentration of hydrogen in the charged samples whose X-ray spectra were taken.

§ 6. THE THERMAL EXPANSION OF PURE PALLADIUM

Pure palladium powder was prepared from material the purity of which was not less than 99·9 per cent, and this was annealed *in vacuo* for 3½ hours at 450° C. A number of photographs were taken at various temperatures over the range from 10 to 300° C., when the specimen was mounted on the focusing camera enclosed in an evacuated chamber. These photographs yielded sharp lines which could be measured to a high degree of accuracy. The temperatures were measured by means of copper-constantan and nickel-nichrome thermocouples which had already been calibrated. The K_α radiation of copper was used, and the indices of the reflexions obtained were 422. The values of the parameters at various temperatures are shown in table 3.

Table 3

Film number	Temperature (° C.)	Parameter (A.)
1	10	$3{\cdot}8820_9$
2	11	$3{\cdot}8822_5$
3	10	$3{\cdot}8820_1$
6	10	$3{\cdot}8820_1$
10	64	$3{\cdot}8846_0$
29	110	$3{\cdot}8869_1$
7	132	$3{\cdot}8879_6$
8	181	$3{\cdot}8905_3$
28	217	$3{\cdot}8922_7$
4	231	$3{\cdot}8928_9$
5	286	$3{\cdot}8957_0$

These figures yield a value for the mean coefficient of thermal expansion over the range 0–300° C. of $12{\cdot}7 \times 10^{-6}$. The corresponding value calculated from the figures given in the *International Critical Tables* is $12{\cdot}33 \times 10^{-6}$. The experimental and calculated coefficients at 20° C. are respectively $11{\cdot}75 \times 10^{-6}$ and $11{\cdot}8 \times 10^{-6}$, which are in good agreement.

§7. THE DEGASSING AND ANNEALING OF CHARGED PALLADIUM SPECIMENS

In the course of the investigation each specimen powder was used several times, and in order to ensure that the effect observed should be that corresponding to the conditions obtaining in any particular experiment and not to those obtaining in previous experiments, it was essential to degas the powder and treat it thermally in such a manner as to bring it back to a standard state before the commencement of each experiment.

Previous workers have found that the hydrogen is liberated if a charged specimen is heated at approximately 150° C. in a maintained vacuum. That this is so may be demonstrated by enclosing the specimen in a glass tube and connecting it to the hyvac pump. The hard note of the pump is modified as soon as the flame of a match is applied to the tube. Not only is it important to know that all the gas has been removed, but it is equally important to know that the material has regained its normal state of equilibrium and is free from distortion. The X-ray method of investigating the degassing conditions supplies information on both of these points, and on that account is superior to other methods employed for the purpose.

A thorough investigation was carried out on this point and many photographs were taken of a specimen after various heat treatments. A specimen maintained at 100° C. and charged with hydrogen at a pressure of 76 cm. of mercury for three hours yielded a photograph, taken at room-temperature *in vacuo* with the focusing camera, which showed an unresolved band reflected from the β phase, the parameter being about 4·03 A. The specimen was heated *in vacuo* at 250° C. and photographed every half hour for the first 1½ hours. At the end of the first half hour it showed an unresolved band corresponding to the α phase, the parameter being 3·8819 A. The appearance of the band did not alter after 1½ hours' heating. The temperature was then raised to 290° C. and the specimen heated for various periods. After 4 hours' heating at 290° C. the band showed signs of resolution. After a further 5½ hours' heating the $K_{\alpha 1}$ could be distinguished from the $K_{\alpha 2}$ line, but the resolution was not good. After 6½ hours' further heating at 290° C. the $\alpha 1$ and $\alpha 2$ lines were separated. Satisfactory resolution of the doublet was not obtained until the specimen had been heated *in vacuo* at 290° C. for about 24 hours. The parameter calculated from the measurement of the resolved doublet, namely 3·8820 A., did not differ from the parameter deduced from the unresolved band photographed after half an hour's heating *in vacuo* at 250° C., indicating that all the gas had been removed by this amount of heating but that the distortion brought about by the occlusion of hydrogen in the palladium had not been removed. To remove this distortion a much longer period of heating was required.

The next operation was to charge the palladium powder, maintained at 100° C., with hydrogen at a pressure of 66 cm. of mercury for half an hour. After evacuation of the chamber, the specimen being still maintained at 100° C. as in the previous instance, the unresolved band appearing on the photograph yielded a parameter of 4·07 A. The specimen was then heated for 1 hour at 450° C. *in vacuo* and an exposure was taken at 18° C. *in vacuo*. The doublet was as well resolved after this treatment as after 24 hours at 290° C., and on measurement it yielded a parameter of 3·8825 A. A further treatment of 2½ hours at 450° C. was more than ample to give complete resolution.

In those cases in which the adsorption caused an expansion of the lattice without change of phase, the doublets were in general well resolved, but they showed a certain lack of definition which was probably due to the distortion of the lattice. It was found that annealing for one hour at 450° C. was sufficient again to produce well defined lines. Linde and Borelius(4) state that in all their exposures the specimen was previously heated at 250° C. in air for 4 hours and that from the photographs taken they concluded that this treatment was sufficient to render the specimens free of hydrogen. The experiments that have just been described show, however, that the specimen was free from gas after being heated *in vacuo* at 250° C. for half an hour, but that heating the specimen for 29 hours at 250° C. *in vacuo* was not sufficient to remove the lattice-distortion caused by the occlusion of the hydrogen in the specimen. The results are important in that they throw some light on the mechanism of absorption and desorption. It appears that the absorbed hydrogen atoms push the palladium atoms farther apart and that in this state the palladium atoms take up positions that are slightly different from those occupied by the atoms in the normal face-centred lattice. Thus, the value of the crystal spacing given by the ordinary Bragg equation no longer has a singular value, and the reflexions of the $K_{\alpha 1}$ and $K_{\alpha 2}$ wave-lengths overlap on the film and give the unresolved band already mentioned. When the specimen is heated at 250° C. *in vacuo* the gas present in the lattice is very easily removed, but though the cause of the displacement of the metallic atoms has been removed the temperature of 250° C. is too low to produce sufficient thermal agitation to cause the palladium atoms to resume their true positions of equilibrium in a reasonable time. The higher temperature of 450° C. however brings the metal to its state of equilibrium in three hours. It is interesting to note in this connexion that palladium powder on which cold work has been done in the filing process, and which gives a band showing lack of resolution comparable to that produced by occluded gas, requires to be annealed at 450° C. for about 3 hours to remove distortion caused in the filing process.

The results of Nähring's(14) investigation of the variation in the width of the X-ray spectral lines of palladium with electrolytic charging and discharging are now readily understood. Nähring obtained an unresolved doublet on charging electrolytically. He observed that if the charged specimen were degassed by making it the anode of an electrolytic cell the increase in line-width produced by the charging was not reduced no matter how long a time for degassing was given. The doublet remained unresolved. He observed also that during anodic degassing the line-width of the second phase remained constant and had the same value as on charging. This was not so for the first phase, for which the line-widths during the discharging were greater than during charging. He found that if the degassing were continued for such a long time that the adsorbed gas was completely removed, as was shown by the return of the lattice-parameter to its original value, the width was still greater than that of uncharged palladium and the doublet remained unresolved. The explanation of these results is that the anodic degassing at room-temperature caused the hydrogen to be removed from the lattice and the mean parameter to assume its original value, but the temperature was not high enough to remove the distortion of the lattice.

§ 8. THE TREATMENT OF THE SPECIMEN BEFORE AND AFTER EXPOSURE TO X RAYS

The method of admitting the hydrogen and of heating the specimen underwent several changes during the course of the work, but in all cases the enclosure was evacuated immediately after exposure and the powder maintained at a temperature of 250° C. for at least 30 min. *in vacuo* to remove the adsorbed gas. During an exposure the temperature was frequently checked and adjusted if necessary. At all temperatures the variation from the required value was not more than 1 per cent as registered on the galvanometer scale.

The greatest difficulty with the apparatus was to render it vacuum-tight. Some exposures had to be made with hydrogen at a pressure of a few millimetres of mercury and a temperature had to be maintained constant for some hours. Under such conditions it was difficult to be free entirely from leakage into the apparatus. To diminish the effect of any slight leakage, a reservoir of about 6 litres capacity was connected to the enclosure and by this expedient the gas pressure could be maintained without appreciable change over long periods.

Three different methods were employed to charge the specimen with hydrogen. In method (1) the hydrogen was admitted into the evacuated enclosure and reservoir to approximately the desired pressure, the temperature being then raised to its proper value and the pressure finally adjusted. The {pressure, concentration} isothermals of Hoitsema and Roozeboom show that, when the gas is admitted at room temperature, the concentration in the specimen almost immediately reaches a value of the order of 0·6 H/Pd, when the β phase is formed. As the temperature is raised to its final value, say 100° C., the concentration gradually adjusts itself to the value corresponding approximately to the final pressure and temperature. If, under these conditions, the α phase existed alone it was found that the doublet could not be resolved, owing to the fact that the β phase had been in existence at room temperature; although the lattice parameter had assumed the value corresponding to the final conditions, distortion was still present. The method was discarded for this reason. In method (2) the temperature of the specimen was adjusted to the desired value *in vacuo* and the gas was admitted in small volumes until the desired pressure was reached. The temperature dropped rapidly over the first few minutes and was adjusted to its proper value after each small addition of gas. On a few occasions, however, at very critical pressures, the temperature was not controlled successfully enough and the α-phase doublet was unresolved. In method (3) the gas was admitted as in method (2), but the temperature in the steady state was approached from the high-temperature side, the temperature of admission being consistently 20° C. higher than the steady-state value. The time taken to cool to this latter value was usually about 15 minutes. In both methods (2) and (3) the concentration of hydrogen in the specimen was being gradually increased, in correspondence with the ascending isothermals of Hoitsema and Roozeboom and of Lambert and Gates. An investigation of the effect of the temperature of admission on the lattice parameter showed that within experimental error the parameter was independent of that temperature.

It may perhaps be desirable to point out here that the term "steady state" is applied to the system when the values of the temperature and pressure during an experiment remained constant. It should not be confused with the term "equilibrium state", which applies to the specimen.

§ 9. THE OCCLUSION OF HYDROGEN BY SILVER

It was important to investigate the occlusion of hydrogen by silver, because this metal was to be used to calibrate the heater of the spectrum camera. The investigation was carried out with a focusing camera, measurements of the parameter of silver being made over a temperature-range from 15° C. to 140° C. and over a pressure-range of 0 to 76 cm. of mercury. The gas was admitted at the temperatures given in column 3 of table 4.

Table 4

Film number	Pressure of hydrogen cm. Hg	Temperature (° C.)	Parameter in hydrogen (A.)	Parameter *in vacuo* (A.)	Occlusion effect (A.)
232	0	16	—	$4\cdot0769_2$	0·0001
235	57·5	15	$4\cdot0768_1$		
240	76	15	$4\cdot0769_7$		
238	76	15	$4\cdot0767_0$		
		Mean	$4\cdot0768_2$		
234	0	140	—	$4\cdot0868_0$	0·00007
236	57·5	140	$4\cdot0866_6$		
239	76	140	$4\cdot0866_4$		
242	76	140	$4\cdot0867_8$		
		Mean	$4\cdot0867_3$		
233	0	100	—	$4\cdot0836_8$	$0\cdot0002_5$
235	57·5	100	$4\cdot0835_2$		
237	76	100	$4\cdot0832_4$		
241	76	100	$4\cdot0835_4$		
		Mean	$4\cdot0834_8$		

Copper radiation was used throughout, the reflections from the silver being 333 and 511. The parameter values are probably accurate to within ±0·0003 A. It will be observed from the last column of the table that the effect of adsorption on the lattice parameter of silver is well within limits of experimental error. Silver could therefore be used for temperature calibration even when surrounded by an atmosphere of hydrogen.

§ 10. PARAMETER-MEASUREMENTS AT VARIOUS TEMPERATURES AND PRESSURES

The first set of parameter-measurements was deduced from spectra taken at a temperature of 100° C. with the focusing camera, the gas being admitted as described under method (2) above. Copper K_α radiation was used for most of the exposures, the reflexions being 422.

To find the length of time necessary to allow the material to reach a state of equilibrium, the lattice parameter of the charged palladium was measured after various intervals of time during which the pressure of the gas in the enclosure and the temperature of the specimen were maintained constant. At a pressure of 16 cm. of mercury, when the times in the steady state were 30 and 60 min. respectively, the parameters had identical values 3·8910. At a pressure of 17 cm. of mercury the parameters were 3·8911, 3·8914 and 3·8912, corresponding to times of 30, 40 and 55 min. respectively in the steady state. The differences between these values were within the limits of experimental error and it was therefore inferred that equilibrium was attained after 30 min. in the steady state. Similar observations at higher pressures, when the β phase was observed, led to the same conclusion, but owing to lack of definition the measurements made on the spectral lines from this phase were not as satisfactory as on those from the α phase. For instance at a pressure of 66 cm. of mercury the parameters found were 4·027, 4·026, 4·024 and 4·027, corresponding to times in the steady state of 30, 60, 60 and 180 min. respectively. These values agree within the limits of accuracy of 0·004 A. which are claimed for these measurements on the β phase.

The results yielded by photographs taken at a pressure of 26 cm. of mercury are of interest. One film showed a strong band from the β phase corresponding to a parameter of 4·019 A. together with a faint line due to 422 reflections of the α phase which gave a parameter value of 3·892 A. Another film which was taken under the same experimental conditions showed only the α phase line, the corresponding parameter being 3·8914 A. Another exposure taken under similar conditions of charging when the specimen was kept for 270 min. in the steady state prior to making the exposure, also showed the lines of the α phase, the parameter being 3·8914 A., and again there was no indication of a reflection from the β phase. The parameters of the α phase however were identical after the pressure and the temperature had been maintained constant for periods of 30 and 270 min. respectively. A satisfactory explanation of the appearance and non-appearance of the β-phase band under apparently the same experimental conditions could not at this stage be given. The matter will be referred to and an explanation will be given in a later paper.

At present it suffices to record that two face-centred lattices of widely differing parameters coexisted at certain temperatures and pressures and no intermediate parameter values were observed. Ubbeholde(15) has pointed out that this absence of intermediate values may be fortuitous and may be due to insufficient precaution against poisoning of the specimen. Every precaution was taken to avoid such poisoning, and the fact that palladium specimens which were newly prepared, and also those which had been used several times over, yielded points falling on the same curve provided evidence that there were no serious errors arising from contamination.

Before proceeding, a detailed investigation was made of the factors governing the values of the lattice parameter. It was found that the parameter was independent of (1) the wave-length of the radiation employed, (2) the atomic planes which were effective in reflecting the incident beam, (3) the temperature of admission of the gas, (4) the rate of cooling from the temperature of admission to the final steady temperature, and (5) the time during which the specimen was kept in the steady state before the exposure was made, provided it exceeded a certain minimum value. The results indicated that the parameter at a given temperature was dependent only on the pressure of the gas surrounding it.

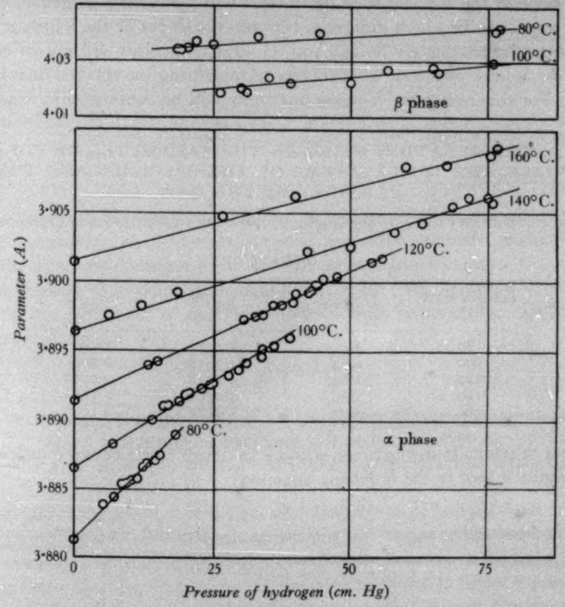

Figure 2.

Attempts were made to find what relation, if any, existed between the parameter of charged palladium and the pressure of the surrounding gas. For this purpose investigations at different temperatures were conducted along the same lines as that carried out at 100° C., the temperatures chosen being 80, 120, 140 and 160° C. When the parameter was plotted against the pressure it was found that the best graphical representation at each temperature was a straight line, both for the α and for the β phase. The results are shown in figure 2, the curves in which have been displaced relative to one another for clearness of presentation. The parameters along the ordinate axis in the diagram refer to the curves at 100° C. At zero pressure the α-phase parameters are 3·8854, 3·8864, 3·8874, 3·8884 and 3·8894 at the temperatures 80, 100, 120, 140 and 160° C. respectively. The parameters of the β phase at a pressure of 25 cm. of mercury are 4·026 and 4·019 at 80 and 100° C. respectively.

The slope of the α-phase lines diminishes with increasing temperature. There does not appear to be much difference between the slopes of the β lines at the two temperatures taken, namely 80 and 100° C., but these lines are not so definitely fixed as the α lines owing to the difficulty of measuring the spectral lines from the β phase. For this reason the α-phase lines only will be considered in detail here.

§ 11. THE RELATION BETWEEN THE PARAMETER OF THE α PHASE, THE TEMPERATURE OF THE SPECIMEN AND THE PRESSURE OF THE GAS

Table 5 gives the values of the slopes of the α curves at the various temperatures.

Table 5

Temperature °C.	$\frac{da}{dp}\times 10^5$	$\log\frac{da}{dp}$	$\log t$
80	39·0	$\bar{4}$·5911	1·9031
100	24·3	$\bar{4}$·3856	2·000
120	18·4	$\bar{4}$·2648	2·0792
140	12·0	$\bar{4}$·0792	2·1461
160	10·4	$\bar{4}$·0170	2·2041

The linear relations found between p and a in figure 2 and between $\log da/dp$ and $\log t$ in figure 3 lead to the following equation:

$$a=a_0(1+\alpha t)+2\cdot5\,pt^{-2} \qquad \text{......(1),}$$

where a is expressed in angstroms, p in cm. of mercury and t in degrees Centrigrade.

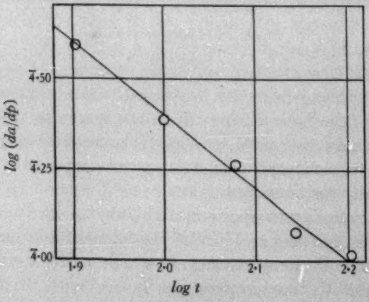

Figure 3.

Hence for the α phase, that is the palladium-rich phase, the change in the parameter of palladium due to the occlusion of hydrogen is directly proportional to the pressure of the hydrogen and inversely proportional to the square of the temperature of the palladium, i.e. $\Delta a = cp/t^2$. This holds for temperatures ranging from 80° C. to 160° C.

Table 6 gives the values of the parameter as calculated from equation (1) and as read off the graph for various arbitrary values of pressure and temperature.

Table 6

t (° C.)	p cm. Hg	$a_0(1+\alpha t)$ A.	$\frac{5}{2}pt^{-2}$ (A.)	a, calculated A.	a, from graph A.
80	15	3·8854	0·0061	3·8915	3·8915
100	30	3·8864	0·0075	3·8939	3·8939
120	30	3·8874	0·0052	3·8926	3·8930
140	50	3·8884	0·0064	3·8949	3·8950
160	50	3·8894	0·0049	3·8943	3·8947

The difference between the calculated and observed values is within the limits of experimental error claimed in the measurement of the parameter, namely ± 0·0004. Equation (1) seems therefore to fit the observations satisfactorily.

The relation also yields information concerning the variation of the rate of change of the parameter of charged palladium with temperature. Differentiating equation (1) we get

$$\frac{1}{a_0}\frac{da}{dt} = \alpha - \frac{5p}{a_0 t^3} \qquad \text{......(2),}$$

where the quantity a_0 is the value of the parameter of pure palladium *in vacuo* at 0° C. The second term on the right-hand side of the equation shows the effect of the occlusion of hydrogen by the palladium on the thermal expansion of the material.

If instead of the pressure of the gas surrounding the palladium the concentration of the gas in the palladium is taken, the relation between parameter and temperature at concentrations not exceeding 10 atomic per cent of hydrogen, and over the range of temperature between 80 and 160° C., is linear as shown in figure 4. Values of the rate of increase of parameter with temperature at the different concentrations are given in table 7.

Table 7

Hydrogen content (atoms per cent)	$\frac{da}{dt}$
0	50×10^{-6}
3·5	78×10^{-6}
5·0	90×10^{-6}
7·5	98×10^{-6}

The absolute values of the slopes of the lines in figure 4 are not accurate, but the curves serve to show that the rate of expansion of the lattice with temperature increases as the hydrogen-content increases. It would appear that the entrance of the hydrogen atoms into the lattice, even though they enter it interstitially, loosens the bonds between the palladium atoms, thus allowing the latter to separate more readily under the action of heat.

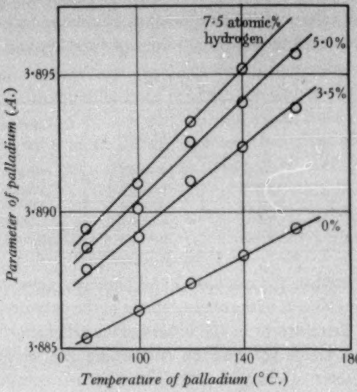

Figure 4.

§ 12. ACKNOWLEDGEMENT

We have pleasure in thanking the Department of Scientific and Industrial Research for a grant which enabled us to carry out the work.

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THE PALLADIUM-HYDROGEN SYSTEM

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Received 4 *June* 1937.

ABSTRACT. The hysteresis effect observed in the palladium-hydrogen system when the pressure of the gas is taken through a cycle of changes has been examined by the X-ray method. Measurements of the parameter of charged palladium at different pressures were made when the temperature was kept constant. When the pressure was increased and the temperature kept at 100° C. the α phase appeared alone up to a pressure of about 20 cm. of mercury, the parameter increasing as the pressure was increased. Between pressures of 20 and 45 cm. of mercury the α and β phases appeared together and on further increase of pressure the β phase appeared alone. With decreasing pressures, starting from an initial pressure of 66 cm. of mercury, the β phase appeared alone until a pressure of about 21 cm. of mercury was reached. Over the range of pressure from 21 to about 17 cm. of mercury the α and β phases appeared together, but at a pressure of 17 cm. of mercury the β phase disappeared, the α phase remaining alone until the pressure was reduced to zero. Those parts of the ascending or descending isothermals in which a single component existed, could be retraced by altering the pressure but this reversibility disappeared when the second component made its appearance.

The concentration of hydrogen in palladium changed rapidly when the β phase appeared or disappeared. The measurements support the view that the palladium-hydrogen system consists of two solid solutions at the two temperatures chosen, namely 100° and 120° C., the hydrogen rich phase being closely associated with the combination Pd_2H, which is capable of taking hydrogen into solution.

The β phase lattice was always found to be distorted; every attempt to obtain this phase free from distortion failed. No such distortion was found with the α phase. The distortion of the β phase lattice remained after the gas had been removed from the metal. It required a temperature well above that necessary to displace the hydrogen from the metal to remove the distortion. It is concluded that the gas is not in its normal state when it leaves the metal.

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§ 1. INTRODUCTION

In a previous paper(1) the effect of pressure and temperature on the occlusion of hydrogen by palladium was studied. The change in the parameter of palladium due to occlusion of hydrogen was found to vary directly as the pressure of the hydrogen and inversely as the square of the temperature of the palladium. In the paper reference was made to the work of Lambert and Gates(2) who found that the relation between the pressure of hydrogen surrounding the palladium at any temperature and the concentration of the gas in the palladium depended upon whether the pressure of the gas was increased or decreased to its final value. The ascending isothermal differed in shape from the descending isothermal, thus exhibiting a cycle similar to a hysteresis loop. In the present paper this effect is studied in detail by X-ray analysis.

The results of Hoitsema and Roozeboom(3) indicated the existence of two immiscible solutions of hydrogen in palladium. Their curves were of the same general shape as those of the ascending isothermals obtained by Lambert and Gates who, however, found a number of factors which had a profound effect on the equilibrium of the system. The last named authors observed, in addition to the hysteresis effect already noted, that the shape of the ascending isothermal depended upon the method adopted to vary the pressure. Thus the curve obtained when the pressure was increased in a regular manner differed from that obtained by alternately adding and withdrawing from the reaction vessel known quantities of hydrogen, the quantities added being always greater than those withdrawn. Whereas a smooth curve could be drawn through the points connecting equilibrium pressure and concentration in the first case, no such smooth curve could be drawn in the second case. Also it was found that if the controlled temperature of the system was allowed to fall to that of the room and was restored after some hours to its original value, the new equilibrium pressure differed appreciably from the original value and no tendency was noted for this pressure to attain its former value even on long standing. The general conclusion reached by these authors is that the ascending isothermals, even for identical experimental conditions, are not repeatable, whilst the descending isothermals are. These results were considered by the authors to indicate the existence of at least two allotropic forms of metallic palladium which probably differed in their rate of adsorption of hydrogen.

A great change in concentration for a small change in pressure was found in the descending isothermals obtained at 75, 103 and 120° C. This took place at each temperature at a concentration of approximately two atoms of palladium to one of hydrogen. In view of the comparatively wide range of temperature over which this effect occurred, it might be considered evidence of the existence of the compound Pd_2H.

The {pressure, concentration} isothermals of the palladium-hydrogen system obtained by Hoitsema and Roozeboom are reproduced in figure 1 together with the descending isothermal at 100° C. (represented by the dotted line) obtained by Lambert and Gates.

§ 2. APPARATUS AND EXPERIMENTAL PROCEDURE

Two cameras, the focusing camera and the fibre camera, were employed in the investigation as explained in our previous paper.

The method of temperature measurement was different in the two cameras. In the focusing camera the temperature of the specimen at any instant could be estimated from the galvanometer deflection. The variation in temperature during the admission of the gas was no more than ± 1° C. With the fibre camera no visible control of temperature was possible. The current through the heater required to produce a given temperature varies with the gas pressure and in consequence it is difficult to maintain a steady temperature whilst the pressure is being altered. An attempt was made to overcome this difficulty by increasing the pressure very slowly and at the same time increasing the heating-current as required by the calibration curve. A similar method was also used when the pressure was decreased. After some practice, it was possible to maintain a fairly constant temperature during the admission of the gas, but owing to the difficulties involved it was not as constant as that obtained with the focusing camera when the temperature could be controlled by keeping the galvanometer spot steady.

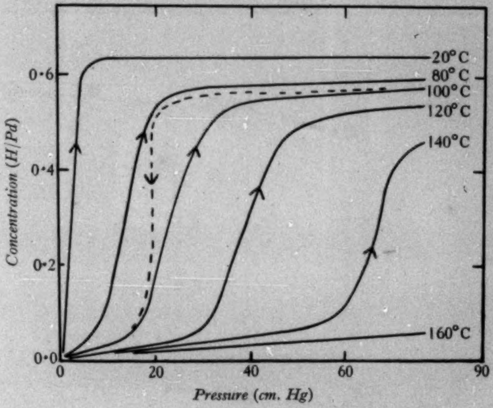

Figure 1.

The first temperature chosen was 100° C., the gas being admitted slowly into the evacuated chamber enclosing the camera until the desired pressure was reached; the temperature of the palladium was maintained at this value throughout the operation. The pressure was kept constant at its final value for 2 hr. before exposing the specimen to the X-ray beam.

The initial part of the investigation was carried out with the focusing camera and it was found that at certain pressures only the α phase was recorded. At higher pressures both the α and the β phases were recorded together and at still higher pressures the β phase was recorded alone. Although the estimated values of the lattice parameter calculated from measurements made on films taken with the focusing camera were more accurate than those calculated from the spectrum photographs obtained with the fibre camera, yet the latter proved more suitable for the work in hand as the structure could continuously be kept under observation. The spectra showed that the structure of the charged palladium remained unchanged as the concentration was varied; they also showed more definitely than the focusing-camera photographs when the β phase made its first appearance. For the latter part of the work, therefore, the fibre camera was almost exclusively used.

§ 3. RESULTS

(i) *The ascending isothermal at* 100° *C.* The first six films reproduced in figure 2 show very clearly what takes place when the pressure of the gas is gradually increased to its final value and kept at this value for 2 hr. before making the exposure. The temperature was maintained at 100° C. throughout these changes of pressure.

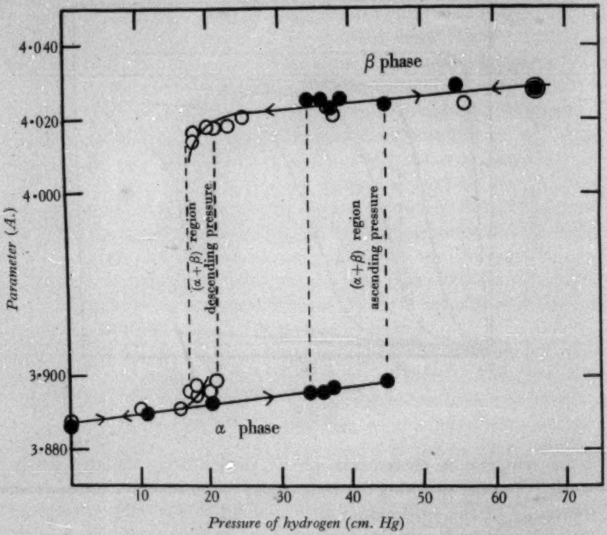

Figure 3. ● ascending pressure; ○ descending pressure.

Up to a pressure of about 20 cm. of mercury only the α phase appears, and if this pressure is not exceeded the curve is retraced on lowering the pressure, that is, the change is reversible. When the pressure is increased to about 34 cm. of mercury, the α and the β phases appear together and they are both present until the pressure is increased to about 45 cm. of mercury. Beyond this pressure only the β phase appears.

(ii) *The descending isothermal at* 100° *C.* To obtain the descending isothermal the pressure of the hydrogen was initially fixed at 66 cm. of mercury and maintained at this value for 2 hr. The pressure was then decreased gradually to a definite value in the range of pressure between 56 cm. and about 0·001 mm. of mercury,

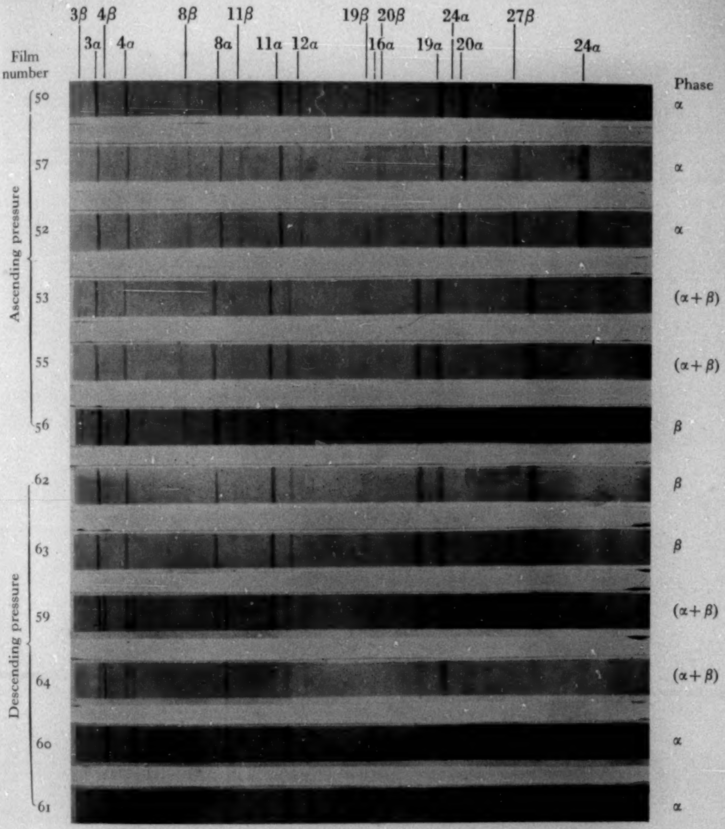
3β
4β
8β
11β
19β
20β
24α
27β
3α
4α
8α
11α
12α
16α
19α
20α
24α
Film number
Phase
Ascending pressure
Descending pressure
50
57
52
53
55
56
62
63
59
64
60
61
α
α
α
(α+β)
(α+β)
β
β
β
(α+β)
(α+β)
α
α

Figure 2.

and maintained at this value for 2 hr. before making the exposure. The temperature was kept at 100° C. as near as possible while the pressure was changed.

When the final pressure was reached in the manner just described, it was found that the β phase appeared alone in the range of pressure between 56 cm. and about 21 cm. of mercury. Over the range from 21 cm. to about 17 cm. the two phases appeared together, but at 17 cm. the β phase disappeared, the α phase remaining alone until the pressure was reduced to zero. Here is a definite indication of the hysteresis effect which had already been observed by Lambert and Gates. The results now obtained are shown in figure 3.

It is of interest to note that only those parts of the ascending or descending isothermal, where a single component exists, could be retraced by altering the pressure; this reversibility disappears immediately the second component makes its appearance.

The values of the lattice parameters of charged palladium after various changes in pressure of the surrounding gas when the temperature of the specimen was kept at 100° C., are collected in table 1.

Table 1. Parameters of charged palladium at 100° C.

	Film no.	Charging pressure maintained for 2 hr. (cm. Hg)	Final pressure for descending isothermal (cm. Hg)	Time in steady state for descending isothermal (hr.)	Parameters (A.)	
					α	β
←Ascending pressure→	50	0·0	—	—	3·8863	—
	57	10·8	—	—	3·8900	—
	52	20·2	—	—	3·8930	—
	105	34·0	—	—	3·8952	$4{\cdot}025_6$
	102	36·0	—	—	3·8954	$4{\cdot}025_6$
	53	37·5	—	—	3·897	$4{\cdot}022_9$
	55	38·7	—	—	Faint	$4{\cdot}025_6$
	103	39·0	—	—	3·896	$4{\cdot}025_6$
	104	45·0	—	—	Very faint	$4{\cdot}024_0$
	69	55·0	—	—	—	$4{\cdot}029_1$
	56	66·0	—	—	—	$4{\cdot}028_1$
←Descending pressure→	62	66·0	56·0	2	—	$4{\cdot}024_1$
	63	66·0	37·7	2	—	$4{\cdot}021_0$
	58	66·0	37·0	2	—	$4{\cdot}023_0$
	90	66·0	25·0	4	—	$4{\cdot}020_3$
	319	66·0	20·0	5	3·896	4·018
	320	66·0	20·0	21	3·896	4·018
	321	66·0	20·0	72	3·896	4·018
	70	66·0	21·0	2	3·899	$4{\cdot}018_0$
	59	66·0	18·0	2	$3{\cdot}898_2$	$4{\cdot}014_4$
	91	66·0	18·0	4	$3{\cdot}895_0$	$4{\cdot}016_4$
	92	66·0	17·0	4	$3{\cdot}896_4$	$4{\cdot}016_6$
	64	66·0	16·0	2	$3{\cdot}891_3$	Faint
	60	66·0	10·0	2	$3{\cdot}891_2$	—
	61	66·0	0·0	2	$3{\cdot}888_0$	—

When the intensities of the lines in the spectra were weak, only an approximate value of the parameter could be obtained; in some cases the lines were so faint that no measurement was possible, but the presence of the phase is indicated in the table so that it may be known when the phases appeared together.

There are wide ranges of pressure over which the two phases coexist; the range is wider for the ascending than for the descending pressure curve. The ascending pressure-range is slightly greater than 11 cm. of mercury but the descending pressure-range is less than 9 cm. of mercury. The extent of these ranges might be modified if a different procedure as regards pressure changes and time during which the pressure remains constant, were adopted. Thus, it was found that the system required a longer time to attain an equilibrium state when the final pressure was reached from the low-pressure side than when it was reached from the high-pressure side. Also the relative amounts of the α and β phases when they appeared together depended upon the time of charging or discharging the palladium. For instance, after the specimen had been charged at a pressure of 66 cm. for 2 hr. at 100° C. and the pressure then reduced to 20 cm. and kept at this value for 5, 21 and 72 hr. respectively, the values of the parameters of the α and β phases were the same but the relative intensities of the lines from the phases changed. Whereas at the beginning the lines of the α phase were weaker than those of the β phase, the reverse was the case after the pressure had been maintained constant for a period of 72 hr. These effects are now being investigated in greater detail.

(iii) *The ascending and descending isothermals at* 120° *C.* The results obtained at this temperature were in general agreement with those found at 100° C. but the ranges over which the two phases appeared together both with ascending and descending pressures, were wider at 120° C. than at 100° C. under the same conditions of pressure and time in the steady state. It was again found that the curves obtained when only one constituent appeared were reversible.

§4. DISCUSSION

The curves obtained by Lambert and Gates§ giving the relation between the pressure of hydrogen and the concentration of hydrogen in palladium at 103° C., when the pressure is increased or diminished as already described, are shown in figure 4. The ascending isothermal takes different forms according to the method of charging the specimen, but the shape of the descending isothermal is practically the same for all conditions of charging and at all temperatures, and a sharp bend occurs in these curves at a concentration of about 0·5, that is, when there are two palladium atoms to each hydrogen atom. After this, the concentration decreases very rapidly as the pressure is lowered; it drops from 0·5 to 0·1 H/Pd whilst the pressure changes from about 18 to 16 cm.

In the ascending isothermal the concentration changes rapidly between pressures of about 36 and 70 cm. of mercury. This may vary according to the method adopted to increase the pressure.

Comparing these curves of change in concentration with pressure with those in figure 3 showing the change in parameter with pressure we find that the region where the concentration changes rapidly with pressure corresponds with the regions where the α and β phases appear together. In other words, the increase or decrease in concentration corresponds with the appearance or disappearance of the β phase. And from the parameter-pressure curves of figure 3, we should expect the slope of the ascending isothermal in the critical region to be less than that of the descending isothermal, as is actually the case in the curves of Lambert and Gates.

If then the sudden rise and fall in the concentration may be associated with the appearance and disappearance of the β phase, the β phase disappears when the concentration is 0·5 H/Pd; this is so at all temperatures according to Lambert and Gates and it is quite definite. The concentration at which the β phase makes its appearance in the ascending isothermals is not so definite; at 100° C. it appears with the α phase over a range of pressure which is greater than that observed in the descending isothermal and the range embraces the concentration 0·5 H/Pd.

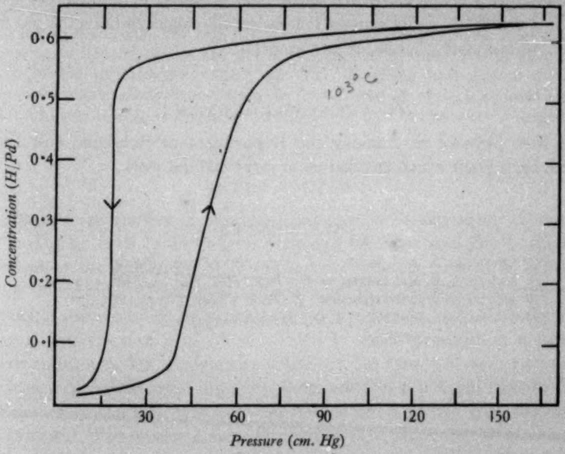

Figure 4.

Since equilibrium is more difficult to attain from the low-pressure than from the high-pressure side, the explanation of the smaller slope of the {pressure, concentration} curve in the critical region of the ascending isothermal may be due to the fact that the state of true equilibrium was not reached. This point needs further investigation. A special apparatus has now been designed to do this.

The disappearance of the β phase at a concentration of two atoms of palladium to one atom of hydrogen would seem to indicate the presence of the compound Pd_2H. The simultaneous existence of both α and β phases would point to duplex regions of solid solutions, which occur at different pressures according as the pressure is increased or decreased to its final value. These facts support the view that the palladium-hydrogen system consists at 100° C. of two solid solutions, the hydrogen-rich phase being closely associated with the combination Pd_2H which is capable of taking more hydrogen into solution.

Another experimental fact to be taken into consideration in arriving at a solution to the problem is the distortion of the β lattice. This was referred to in our previous paper(1). Every attempt to obtain the β phase free of distortion failed. The α phase showed no such distortion up to the highest hydrogen concentrations. Nähring(4) suggested the formation of an orthorhombic lattice, but the results of the present investigation did not confirm this. There is no doubt however, that a distortion of the β lattice takes place, and that the distortion remains after the gas has been removed. The presence of the hydrogen, even though it enters the palladium lattice interstitially, causes a permanent displacement of the palladium atoms which if the concentration is high enough, cannot be removed without subjecting the material to a temperature well above that required to remove the hydrogen from the metal. This would suggest that at certain concentrations the gas may not be in its normal state when it leaves the metal.

§ 5. ACKNOWLEDGEMENT

We have pleasure in thanking the Department of Scientific and Industrial Research for a grant which enabled us to carry out the work.

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THE MAGNETIC PROPERTIES OF IRON AMALGAMS

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Received 6 *May* 1937. *Read in title* 25 *June* 1937

ABSTRACT. Amalgams of iron and mercury have been prepared by electrolysis and the magnetic properties of the frozen amalgams investigated by the Gouy method. Only very minute quantities of iron can possibly be absorbed before ferromagnetic properties are evident in the amalgams. The iron behaves as if it possesses a specific magnetization of 130 c.g.s. units instead of the 220 normally exhibited by pure iron in bulk at the temperature of the experiments, $-78{\cdot}5^\circ$ C. With increasing iron-content the paramagnetism of the amalgam, as distinct from the ferromagnetism of the iron, also increases steadily, for which it is suggested that a combination of iron and mercury is responsible.

§ 1. INTRODUCTION

The magnetic properties of amalgams have not been extensively studied. A few amalgams have recently been examined by Bates and Tai(1), who drew attention to the behaviour of ferromagnetic materials present as impurities in mercury amalgams. Although its effects may be of considerable importance when precision susceptibility measurements are being made, little is known about the magnetic behaviour of iron when it exists in small quantities in a para- or diamagnetic substance. On the evidence obtained from a study of copper amalgams in which iron was present as an impurity, Bates and Tai concluded that the ferromagnetic nature of the iron was only apparent when a certain concentration of iron was exceeded. The present communication gives an account of an examination of the magnetic properties of mercury amalgams containing small known quantities of iron.

Some of the physical properties of iron amalgams have been studied by Rabinowitsch and Zywotinski(2), who emphasized that it is extremely difficult to cause iron to enter into solution in mercury. They considered that the iron behaves as if it were in a colloidal state or, at any rate, as if it were dispersed throughout the mercury in the form of small particles, which ascend to the surface at rates determined by Stokes's law. They found that it is possible to remove practically all the iron from an amalgam by the application of a magnetic field, an observation which was often confirmed in the course of the present work. When a vertical tube containing an iron amalgam is allowed slowly to descend between the poles of an electromagnet the iron is pulled to the surface of the amalgam, and when the tube is lowered until the amalgam surface no longer lies between the pole pieces, a drop of amalgam is detached from the surface. By lowering the tube still further the drop can be moved to any distance from the surface of the amalgam and can be held in the field for an indefinite period, while mercury drips slowly away from it until only a small quantity remains. The residual drop contains nearly all the iron previously put into the amalgam, and it is hoped later to use this method of separation in the preparation of highly concentrated amalgams. The rate at which iron can thus be drawn to the surface of an amalgam is quite remarkable.

§ 2. METHOD AND PREPARATION OF AMALGAMS

In view of the facts outlined above it is clearly impossible to make susceptibility-measurements with liquid amalgams by means of an electromagnet used in the ordinary way. In the present work the amalgams after thorough mixing by agitation were frozen, and the susceptibilities of the solid amalgams were then determined. The mercury used was Analar mercury which, for our purposes, was not considered to need any further purification. The amalgams were all prepared by electrolysis with the complete denudation of a solution of ferrous sulphate of known iron-content, to which a small quantity of pure sulphuric acid had been added. The anode was a platinum foil and the cathode a pool of mercury of known mass, and currents of from 2 to 4 A. were usually employed with a cathode-area of some 12 cm^2. On completion of the electrolysis the amalgam was rapidly washed with distilled water, partially dried with filter paper and introduced into the bulb *A* of a pyrex glass apparatus of the form shown in figure 1. This was quickly evacuated through a series of drying-tubes attached to a Hyvac pump, and the amalgam was transferred to the uniform tube *C* which was then sealed off at *B*, where a hook for suspending the tube was later made.

The tube *C* was then inverted and rotated many times while wrapped in solid carbon dioxide until the amalgam had solidified, care being taken to freeze the amalgam so that a rod of uniform cross-section and as homogeneous as possible was formed. The tube was then suspended from one arm of a sensitive chemical balance inside a copper tube mounted within a Dewar flask and surrounded with solid carbon dioxide. The latter was placed between the flat pole pieces of an electromagnet, so that the surface of the amalgam lay approximately on the line of centres of the pole pieces. The arrangement is shown in figure 2, a brass tube to protect the suspension from draughts being omitted from the drawing.

Let us suppose that the magnetic pull on the tube and its contents for the field *H* between the pole faces and zero at the lower end of the tube is $\delta m_{0,H}$ when the tube contains pure mercury, and $\delta m_{c,H}$ when it contains an amalgam of concentration *c*. Then, using the modified Gouy formula given by Vogt(3), we have

$$\delta m_{0,H}\, g = \tfrac{1}{2}(k_{\mathrm{Hg}})\, \alpha H^2 \qquad \ldots\ldots(1),$$

and

$$\delta m_{c,H}\, g = \tfrac{1}{2}(k_c)\, \alpha H^2 + \sigma_c \alpha H \qquad \ldots\ldots(2),$$

whence

$$2\,(\delta m_{c,H} - \delta m_{0,H})\, \frac{g}{\alpha H^2} = (k_c - k_{\mathrm{Hg}}) + \frac{2\sigma_c}{H} \qquad \ldots\ldots(3),$$

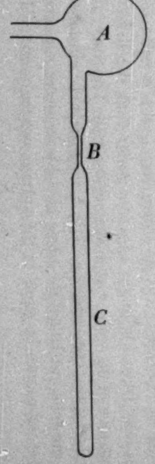

Figure 1. Apparatus for preparation of iron amalgams.

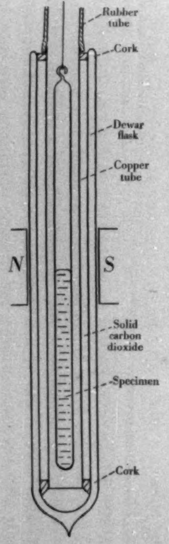
Rubber tube
Cork
Dewar flask
Copper tube
N
S
Solid carbon dioxide
Specimen
Cork

Figure 2. Apparatus for magnetic measurements on frozen amalgams.

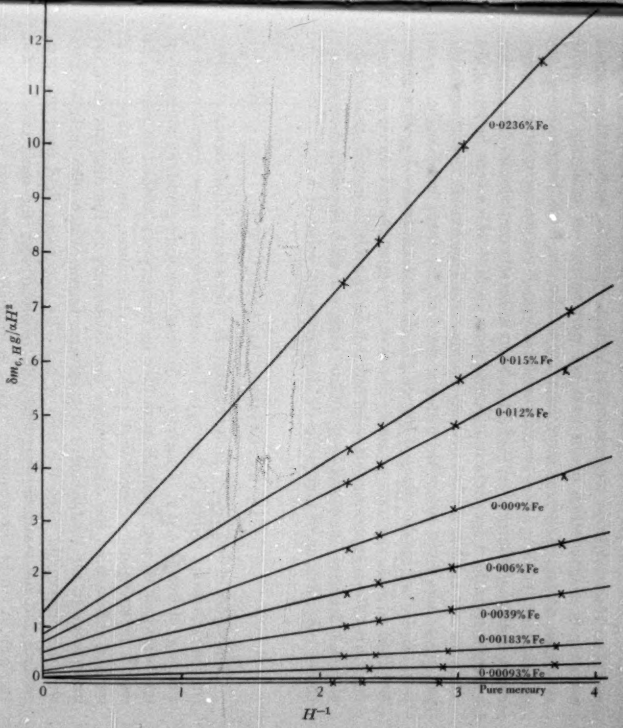

Figure 3. Graphs showing relation between $\delta m_{c,\,H}g/\alpha H^2$ and H^{-1} for a series of iron amalgams of stated concentrations by weight. Ordinates have been multiplied by $9{\cdot}37 \times 10^4$ and abscissae by 14,800 oersted^{-1}.

where k_{Hg} and k_c respectively represent the volume susceptibilities of pure mercury and of an iron amalgam of concentration c, both at $-78\cdot5^\circ$ C., and σ_c is the saturation intensity of magnetization of the iron per unit volume of amalgam. The above equations contain no terms corresponding to the magnetic forces acting upon glass and air, for these forces should vanish because of the symmetry of the arrangement, and this condition was found to obtain in these experiments. The complete equation given by Vogt contains a further term in H^{-2} which is to be introduced when the iron exhibits marked hysteresis properties. This term is usually negligible, and the results given below show that it need not be introduced in the present work, at any rate for the values of H used. In the above equations k_{Hg} is, of course, negative, while k_c is always positive. The field H was measured with a calibrated fluxmeter. From equation (2) it follows that if $\delta m_{c,H}g/\alpha H^2$ is plotted as a function of H^{-1}, a series of linear graphs should be obtained, each line corresponding to a known concentration of iron, while its slope gives the value of σ_c.

§ 3. EXPERIMENTAL RESULTS

The values of $\delta m_{c,H}g/\alpha H^2$ plotted against H^{-1} for a series of amalgams of known concentrations are shown in figure 3. The concentrations range from 0·00093 to 0·0236 g. of iron in 100 g. of mercury. Although we were primarily interested in the behaviour of iron in small quantities in mercury we wished to extend the results to amalgams of somewhat higher concentrations, but the experimental method suffers from the disadvantage that asymmetry in the distribution of the iron results in the establishment of transverse forces, which may make accurate weighing impossible when the field is on. The maximum field used was 7100 oersteds and the maximum magnetic pull recorded with the most concentrated amalgam in a tube approximately 7 mm. in internal diameter was 1·64 g., so that transverse forces could be large. The scope of the work can only be extended by another method which we hope to arrange later. The line for solid mercury corresponds to a value $-1\cdot95\times10^{-6}$ for k_{Hg} or $0\cdot137\times10^{-6}$ for χ_{Hg}, found by comparing the magnetic pulls on a tube containing pure mercury at $-78\cdot5^\circ$ C. and at room-temperature. The values given by Vogt(4) for single crystals of mercury at liquid-air temperatures are $\chi_{\parallel}=-0\cdot112$ and $\chi_{\perp}=-0\cdot121\times10^{-6}$ c.g.s. units for fields parallel and perpendicular to the crystalline axis respectively.

The main experimental difficulty was the obtaining of a uniform distribution of iron throughout the volume of the amalgam, for on repetition of the magnetic measurements after successive mixing and freezing operations very considerable differences were found between the individual values of the magnetic pull for a fixed value of H. Consequently, to obtain $\delta m_{c,H}$ the average of at least eight observations was taken. It might appear *a priori* that the differences seriously limit the accuracy of the work, but this is not the case. The magnetic pull is determined mainly by the concentration of iron in a limited volume of the amalgam situated in the tube just below the edges of the pole pieces, and the concentration here may not, of course, be equal to the average concentration. Hence by taking the mean of many values of the magnetic pull for a chosen value of H we merely ensure that the final result corresponds to the correct value of the total iron-content, provided that there are no marked discontinuities, in the relation between the magnetic properties and the quantity of iron present. Moreover, it was evident that when the individual determinations from which any one graph shown in figure 3 was found, were plotted as a function of H^{-1}, a series of lines with a common intercept on the axis of ordinates was obtained in all cases except that of the most concentrated of the amalgams.

The lines of figure 3 ought all to meet at $H^{-1}=0$ on the line of $\delta m_{0,H}g/\alpha H^2$ against H^{-1}, the horizontal line for pure solid mercury, which lies below the H^{-1} axis, provided that the iron is present in the mercury in a free state—i.e. if the properties of the mercury are unchanged by the presence of iron. This is clearly not so, and all the lines do not meet in a single point when produced. In figure 4 the slopes of the several lines of figure 3 are plotted against the corresponding concentrations, and within the limits of experimental error the resulting graph is practically a straight line intersecting the concentration axis where c equals about 0·00063 g. of iron in 100 g. mercury. We see, then, that for concentrations over 0·001 g. of iron in 100 g. of mercury the magnetic properties of the iron atoms are constant.

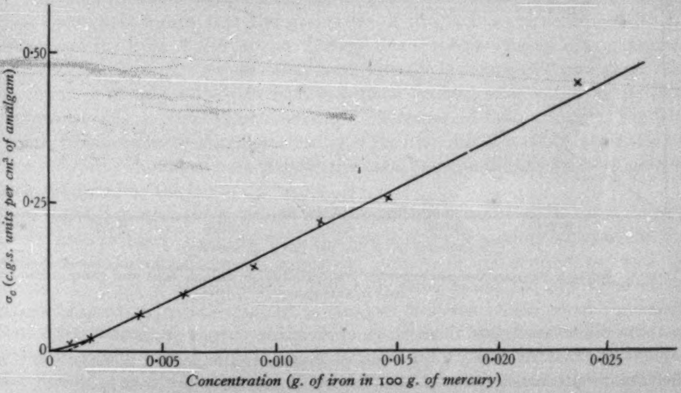

Figure 4. Relation between saturation intensity of magnetization of amalgam and concentration.

Returning to figure 3, we see that k_c, which is measured by the intercept on the axis of ordinates, is also a function of the concentration. In figure 5 the values of these intercepts above the line for pure mercury are plotted against the corresponding values of c. The values are not very accurate, particularly in the cases where c is very low, but we consider the graph, which must pass through the origin, to represent fairly the variation of k_c with c. From it we conclude that the paramagnetism of the amalgam as a whole increases more or less linearly with the iron-content at higher concentrations.

It is of interest to compare the mean value of the specific magnetization of iron in mercury at −78·5° C., obtained from the slope of figure 4, with the value found by direct measurements on iron in bulk. From figure 4 it is found that for iron-concentrations of 0·005 and 0·025 g. in 100 g. of mercury, the respective values of the saturation intensity of magnetization per cm³ of amalgam are 0·0806 and 0·4485 c.g.s. units, or 0·0056 and 0·0315 per gram of amalgam, assuming that in these dilute amalgams there is no appreciable change in density with iron-content, and that the density of the solid amalgam is 14·24 g./cm³ Hence, it follows that the magnetization of 1 g. of amalgam is increased by 0·0259 unit by the addition of 0·0002 g. of iron, whence the specific magnetization of iron in mercury at −78·5° C. is 130 units. Now, the value found by Weiss and Forrer⁽⁵⁾ and amended by Fallot⁽⁶⁾ may be taken to be 220 units approximately, so that each atom of iron dissolved in mercury appears to possess only about 0·59 of the ferromagnetic moment of an atom of iron in bulk at the same temperature.

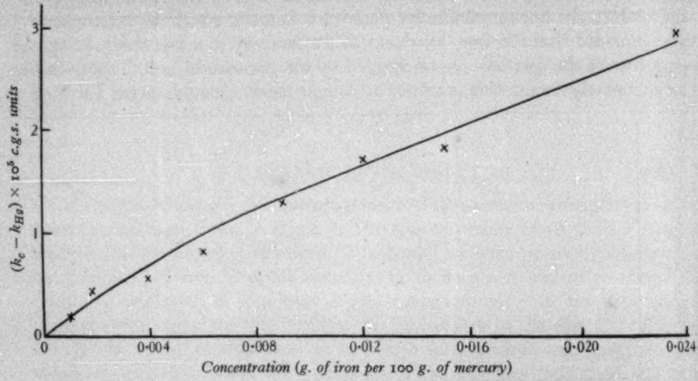

Figure 5. Relation between the paramagnetic susceptibility in infinite field and concentration of iron in amalgam.

§4. DISCUSSION OF RESULTS

The first interesting point which emerges from this work is the minuteness of the quantity of iron which can possibly be absorbed by solid mercury before signs of ferromagnetism occur, for it is known that copper can assimilate small quantities and aluminium quite large quantities before this occurs. It is not generally realized how rapidly the iron in an amalgam is carried to the surface. Indeed, these measurements showed that the Gouy method cannot safely be used with a liquid amalgam, unless either it has first been ascertained that no intensely magnetic constituent is to be found at the surface, or the composition of the amalgam in the immediate neighbourhood of the pole pieces has been specially determined. The latter procedure was adopted by Bates and Tai in the case of manganese amalgams, in which it has recently been found in this laboratory that a strongly magnetic constituent rises to the surface.

A second point is the exactness with which the simple Gouy relation holds, for it means that the iron present was saturated in the technical sense of the term, at any rate in those portions of the field which gave rise to appreciable magnetic pulls. We have already mentioned that when the individual determinations of $\delta m_{c,H} g/\alpha H^2$ for a given amalgam (except in the case of the most concentrated *one* investigated) were plotted against H^{-1}, a series of lines giving the same intercept on the ordinate $H^{-1}=0$ were obtained, although the slopes of the lines varied. This is an important point because it means that the properties of the mercury are changed by the presence of the iron. For it is easy to show that if the paramagnetism represented by the intercept on $H^{-1}=0$ was associated with the ferromagnetic iron alone, then the intercept should vary with each individual determination made on the same amalgam, owing to lack of homogeneity. Moreover, if the paramagnetism were directly proportional to the concentration of the iron, it is also easy to show that the lines of figure 3 should all pass through the same point on the line for solid mercury when produced to the left of $H^{-1}=0$.

We have seen that the intercept for each amalgam has a definite value, and the several lines of figure 3 do not meet in a single point. Therefore we conclude that with increasing iron-content an increasing quantity of iron is combined with the mercury to form a paramagnetic. Hence to some extent the low value of the specific magnetization is explained by the loss of atoms combined with mercury. Now during the electrolysis considerable quantities of hydrogen are evolved, and it is also possible that a combination of iron and hydrogen occurs, or the hydrogen may be occluded in the particles of iron. This too would reduce the value of the specific magnetization. In the case of chromium prepared from chromium amalgams, Bates and Baqi(7) have shown that a ferromagnetic compound of chromium and hydrogen is formed and can only be broken down by heating to about 1200° C. *in vacuo*. The main difficulty in the way of the above explanations is the fact that the percentage of iron atoms which are ferromagnetic in the amalgams is so constant that the explanations virtually amount to the assumption that definite equilibrium compounds of iron and mercury or of iron and hydrogen are formed.

§ 5. ACKNOWLEDGEMENT

The magnetic measurements were made with apparatus purchased in part with a grant to one of us from the Government Grants Committee of the Royal Society.

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THE DIAMAGNETIC SUSCEPTIBILITIES OF DISSOLVED AND HYDRATED SALTS

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Received 28 *April* 1937. *Read in title* 25 *June* 1937

ABSTRACT. From a wide survey of the available experimental data for the diamagnetic susceptibilities of salts in aqueous solution, the effective susceptibilities of the ions in solution are obtained and their additivity is established to within 1 per cent of the observed values. There are shown to be systematic differences between the susceptibilities of ions in solution and in crystals. Small univalent ions and all bivalent ions have effectively smaller susceptibilities in solution than in crystals owing to the effect of the ions on the surrounding water molecules; this effect is correlated with the field at the boundary of the ions. Large univalent ions have effectively larger susceptibilities in solution than in crystals, owing mainly to the change in coordination of these ions when they are dissolved.

New measurements are given of the susceptibilities of a number of hydrated salts. It is shown that the susceptibilities of salts obtained from results for hydrated crystals, by assuming the water of hydration to have the same susceptibility as ordinary water, approximate more closely to the effective susceptibilities of salts in solution than to the true susceptibilities of the anhydrous salts.

§ 1. INTRODUCTION

The effect of solution on the diamagnetic susceptibility of certain salts has been discussed briefly in a previous note(1),* but as the account there given was necessarily very restricted it has been thought worth while to amplify the analysis of the data and also to give the sources from which the values of the susceptibilities were obtained. In addition the discussion has been extended to hydrated salts for which a number of new measurements have been made. Some slight repetition is inevitable in the tabulation of the results if continual reference to the former note is to be avoided, but the method of presentation of the data has been somewhat revised and the significance of the results made clearer by an analytical treatment.

§ 2. SUSCEPTIBILITIES OF DISSOLVED SALTS

The calculation of the susceptibilities of dissolved salts has usually been based on the assumptions that the susceptibility of the solution varies linearly with concentration and that the susceptibility of the solvent is unaffected by the presence of the dissolved salts. The legitimacy of these assumptions must be examined in the light of the experimental data. Weiss (2) has shown that there is probably an appreciable effect due to the action of the dissolved ions on the surrounding water molecules, but he was unable to proceed very far in an attempt to link up this effect with a similar one for refractivities owing to a lack of sufficiently extensive data. Furthermore, there may be mutual effects between ions in solution making the susceptibilities of particular ions dependent upon the other ions present. This may be tested directly by determining whether the susceptibilities are additive within the limits of experimental error, i.e. whether a definite susceptibility can be attributed to an ion in solution independently of the other ions present. The experimental data will be examined with these points in view.

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* This paper will be referred to in the text as "paper I".

The assumption of a linear variation of solution susceptibility with concentration appears to be justified for many simple salts by the results obtained, but that it may not be universally true, has been shown by the work of a number of investigators (3). In fact it would not be expected to be true unless the substance is completely dissociated over the range of concentrations used.*

To examine the other points it is first necessary to obtain the most probable values of the susceptibilities of salts in solution. As the data for solvents other than water are very meagre the discussion will be restricted to aqueous solutions. The majority of measurements have been made for simple salts of the type AB and AB_2 and for the acids HCl, HBr and HI; recent results for these compounds are summarized in table 1. It will be seen that there is reasonably good agreement between the results obtained by different observers, particularly those shown in columns (3) to (6). The occasional divergences of Kido's (4) results, in column (2), are probably due to the use of only one solution-strength for each salt. It should be mentioned, however, that Kido's results for solutions represent only a fraction of the total number of his measurements, the majority of which were made with crystalline powders. The results obtained by Ikenmeyer (5) and given in column (1) of the table often show considerable divergences from those obtained by other investigators and consequently where his is the only available value for a particular salt it must be regarded with caution. In arriving at the most probable values given in the last column, most reliance has been placed on the measurements made by Hocart (6), Abonnenc (7), Frivold and others (8), and Veiel (9); when other measurements are in substantial agreement with the results obtained by these investigators they have been incorporated in finding a mean value. The results used in finding the mean values are indicated by the numbers in parentheses. Susceptibilities dealt with in this paper are all diamagnetic and are given in units of 10^{-6}; i.e. the values quoted have to be multiplied by 10^{-6} to give the diamagnetic susceptibility per gram-molecule.

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* The work of Rao on the Raman spectra of solutions indicates that HNO_3, H_2SO_4 and all oxyacids dissociate progressively with increasing dilution. The halogen acids and salts of the alkali and alkaline-earth metals, apart from acid salts, appear to be fully dissociated even in strong solutions. In the case of the acid salts of the alkali metals there is complete dissociation into the metal ion and the acid radical, but further dissociation of the acid radical occurs with increasing dilution (21).

Table 1. Susceptibilities of salts in aqueous solution, per gram-molecule

Salt	(1) Iken-meyer	(2) Kido	(3) Hocart	(4) Abon-nenc	(5) Frivold and others	(6) Veiel	(7) Other values	(8)	Most probable values
LiF	—	—	—	—	—	—	—	—	—
LiCl	26·8	24·9	—	24·6	24·2	25·1	27·0(10)	25·4(10)	24·7 (2, 4, 5, 6)
LiBr	37·3	—	—	—	36·0	35·9	—	—	36·0 (5, 6)
LiI	55·6	55·8	—	—	—	52·7	—	—	54·2 (2, 6)
NaF	—	—	—	—	—	—	—	—	—
NaCl	30·0	—	30·8	30·1	30·4	30·3	—	—	30·3 (1, 3, 4, 5, 6)
NaBr	43·2	42·9	—	—	—	40·7	—	—	42·3 (1, 2, 6)
NaI	60·4	60·6	—	—	—	59·6	59·1(11)	—	59·9 (1, 2, 6, 7)
KF	—	—	—	24·5	24·1	—	—	—	24·3 (4, 5)
KCl	36·2	—	39·6	39·4	39·4	39·2	—	—	39·4 (3, 4, 5, 6)
KBr	52·6	—	—	—	50·3	50·1	—	—	50·2 (5, 6)
KI	67·8	—	—	—	—	68·0	66·6(12)	—	67·9 (1, 6)
RbF	—	—	—	—	—	—	—	—	—
RbCl	—	—	—	48·1	—	—	—	—	48·1 (4)
RbBr	65·5	—	—	—	—	—	—	—	65·5 ? (1)
RbI	—	—	—	—	—	—	—	—	—
CsF	—	—	—	—	—	—	—	—	—
CsCl	—	—	—	61·4	—	—	—	—	61·4 (4)
CsBr	—	—	—	—	—	—	—	—	—
CsI	92·5	—	—	—	—	—	—	—	92·5 (1)
MgF_2	—	—	—	—	—	—	—	—	—
$MgCl_2$	49·7	49·0	—	49·7	—	—	50·5(13)	—	49·7 (1, 2, 4, 7)
$MgBr_2$	72·2	—	—	—	—	—	—	—	72·2 (1)
MgI_2	111·4	—	—	—	—	—	—	—	111·4 ? (1)
CaF_2	—	—	—	—	—	—	—	—	—
$CaCl_2$	51·2	51·1	55·6	56·2	56·7	55·7	—	—	56·0 (3, 4, 5, 6)
$CaBr_2$	—	—	—	—	78·5	77·3	—	—	77·9 (5, 6)
CaI_2	—	—	—	—	—	111·3	—	—	111·3 ? (6)
SrF_2	—	—	—	—	—	—	—	—	—
$SrCl_2$	61·6	61·3	—	65·2	65·3	64·2	—	—	64·9 (4, 5, 6)
$SrBr_2$	85·3	87·4	—	—	87·9	87·9	—	—	87·7 (2, 5, 6)
SrI_2	131·1	—	—	—	—	123·2	—	—	123·2 (6)
BaF_2	—	—	—	—	—	—	—	—	—
$BaCl_2$	74·0	—	—	77·1	76·3	75·8	—	—	76·4 (4, 5, 6)
$BaBr_2$	103·6	—	—	—	—	100·7	—	—	100·7 (6)
BaI_2	—	—	—	—	—	137·8	—	—	137·8 (6)
HCl	—	21·9	22·0	21·9	—	20·9	21·9(14)	22·0(10) 23·0(15)	21·9 (2, 3, 4, 6, 7, 8)
HBr	—	34·6	—	33·0	—	32·5	32·5(14)	31·4(15)	32·8 (2, 4, 6, 7, 8)
HI	—	53·5	—	48·8	—	50·2	50·2(14)	49·3(15)	49·6 (4, 6, 7, 8)

Table 2. Comparison of susceptibilities with observed values. $\Delta\chi = \chi_{\text{calc.}} - \chi_{\text{obs.}}$

	Chlorides			Bromides			Iodides		
	$\chi_{\text{obs.}}$	$\chi_{\text{calc.}}$	$\Delta\chi$	$\chi_{\text{obs.}}$	$\chi_{\text{calc.}}$	$\Delta\chi$	$\chi_{\text{obs.}}$	$\chi_{\text{calc.}}$	$\Delta\chi$
H	21·9	21·3	−0·6	32·8	32·6	−0·2	49·6	50·4	0·8
Li	24·7	24·8	0·1	36·0	36·1	0·1	54·2	53·9	−0·3
Na	30·3	30·7	0·4	42·3	42·0	−0·3	60·2	59·8	−0·4
K	39·4	39·1	−0·3	50·2	50·4	0·2	67·9	68·2	0·3
Rb	48·1	48·1	0·0	?	59·4	—	—	77·2	—
Cs	61·4	62·4	1·0	—	73·7	—	92·5	91·5	−1·0
Mg	49·7	49·7	0·0	72·2	72·3	0·1	?	107·9	—
Ca	56·0	55·7	−0·3	77·9	78·3	0·4	?	113·9	—
Sr	64·9	65·0	0·1	87·7	87·6	−0·1	123·2	123·2	0·0
Ba	76·4	78·0	1·6	100·7	100·6	−0·1	137·8	136·2	−1·6

From the most probable values of the susceptibilities shown in table 1, the ionic susceptibilities in terms of an assumed value x for the smallest ion H^+ were obtained by a method previously described (table 1 *a*, paper I). These values were obtained by assigning equal weight to the results for all the salts and acids except RbBr, MgI_2 and CaI_2, for which the results are doubtful and were therefore omitted. The additivity principle may be tested by comparing the sums of appropriate ionic susceptibilities with the experimental values. The results of this comparison are shown in table 2.

It will be seen that the difference between the observed and calculated values is generally less than 1 per cent of the observed value, so that the calculations indicate that within the limits of experimental error the susceptibilities are additive.

From the ionic susceptibilities in terms of x the absolute susceptibilities were obtained in the manner explained in paper I and will be found tabulated in tables 1 *b* and 1 *c* of that paper and in table 3 of this. Briefly, the method consisted in assuming that the susceptibilities of the large, singly charged ions Cs^+, Rb^+, Cl^-, Br^- and I^- in solution are in the same ratio as in the corresponding crystalline halides.

§ 3. COMPARISON OF SUSCEPTIBILITIES OF IONS IN SOLUTION AND IN CRYSTALS

The effect of solution on the susceptibility of an ion will in general be different from the effect of packing it in a crystal. The type of variation to be expected has already been discussed qualitatively, in paper I, and it has been shown that there is a difference between the apparent ionic susceptibilities in solution and in crystals. The results are given in table 3, the columns headed χ_s' and χ_c giving the apparent susceptibilities in aqueous solution and in the crystalline state(16) respectively. The difference $\chi_s' - \chi_c$ or $\Delta\chi$ is given in column 6. The main point to be noticed in these values is that $\Delta\chi$ is negative for small and doubly charged ions and positive for large singly charged ions.

The significance of this variation in $\Delta\chi$ is brought out by the following analysis. The true susceptibility χ_s of an ion in solution is to be distinguished from the apparent value χ_s' obtained by assuming the solvent to be unaffected by the dissolved ions. Let χ_w be the susceptibility of pure water and χ_w' the susceptibility of water molecules immediately surrounding or attached to dissolved ions. It will be assumed that only water molecules in immediate contact with a dissolved ion are appreciably affected. If we write

$$\chi_w' = \chi_w + \Delta\chi_w \qquad \text{......(1),}$$

then $\Delta\chi_w$ is the change in susceptibility of water per gram-molecule due to the presence of ions. If $\Delta\chi_w$ is positive the numerical value of the susceptibility of water is increased by the dissolved ions and vice versa. If C is the average number of water molecules attached to a dissolved ion then

$$\chi_s' - \chi_s = C\Delta\chi_w \qquad \text{......(2).}$$

The susceptibility χ_c of an ion in a crystal, or its susceptibility χ_s in a solution differs from that χ_0 of a free ion, owing to the effect of the surrounding atoms or molecules; in general it appears that the susceptibility is numerically greater in the free state than in the crystalline or dissolved state. Hence, if we write

$$\chi_0 - \chi_c = \Delta\chi_0^c \qquad \text{......(3),}$$

and

$$\chi_0 - \chi_s = \Delta\chi_0^s \qquad \text{......(4),}$$

$\Delta\chi_0^c$ and $\Delta\chi_0^s$ will usually be positive quantities. Combining equations (2), (3), and (4) we have

$$\chi_s' - \chi_c = (\Delta\chi_0^c - \Delta\chi_0^s) + C\Delta\chi_w \qquad \text{......(5).}$$

Table 3. Comparison of susceptibilities of ions in solution and in crystals. χ_s', apparent susceptibility in solution; χ_c, susceptibility in crystalline state; R, ionic radius; C, number of water molecules surrounding each ion in solution.

Ion	R (angstrom)	n/R^2	χ_s'	χ_c	$\chi_s' - \chi_c$	C	$(\chi_s' - \chi_c)/C \doteqdot \Delta\chi_w$
H^+	—	—	−3·8	0	−3·8	—	—
Be^{+2}	0·39	13·15	−0·4	0·3	−0·7	4	−0·18
Mg^{+2}	0·71	3·97	−0·5	4·3	−4·8	6	−0·80
Zn^{+2}	0·83	2·90	9 ?	16 ?	−7 ?	6	−1·2 ?
Li^+	0·68	2·16	−0·3	0·7	−1·0	4	−0·25
Ca^{+2}	0·98	2·08	5·5	10·7	−5·2	6	−0·87
Cd^{+2}	1·03	1·88	20·7	24 ?	−3·3 ?	6	−0·55 ?
Sr^{+2}	1·15	1·52	14·8	18·0	−3·2	6	−0·53
Ba^{+2}	1·31	1·16	27·8	29·0	−1·2	6	−0·20
Na^+	0·98	1·04	5·6	6·1	−0·5	4	−0·12
K^+	1·33	0·56	14·0	14·6	−0·6	4	−0·15
F^-	1·33	0·56	10·3	9·4	0·9	4	0·22
Rb^+	1·48	0·46	23·0	22·0	1·0	4	0·25
Cs^+	1·67	0·36	37·3	35·1	2·2	4	0·55
Cl^-	1·81	0·31	25·1	24·2	0·9	4	0·22
Br^-	1·96	0·26	36·4	34·5	1·9	4	0·48
I^-	2·19	0·21	54·2	50·6	3·6	4	0·90
NH_4^+	—	—	16	13·5			
NO_3^-	—	—	20·8	19·6			
ClO_3^-	—	—	32	26			
ClO_4^-	—	—	33	30			
SO_4^-	—	—	43	38			

The main difficulty in applying this equation to the data given in table 3 is that no very reliable estimate can be made of the quantities $\Delta\chi_0^c$ and $\Delta\chi_0^s$. It is probable, however, that these quantities will be of the same sign and of comparable magnitude, so their difference will usually be small. In particular this will be true for the smallest ions which under all conditions have small susceptibilities. Moreover, for these ions we should expect $\Delta\chi_w$ to be largest, which is a further justification for neglecting the first term. Consequently to a first approximation for small and multiply charged ions we may write

$$\chi_s' - \chi_c \doteqdot C\Delta\chi_w$$

or

$$\Delta\chi_w \doteqdot (\chi_s' - \chi_c)/C \qquad \text{......(6).}$$

The fact that $(\chi_s' - \chi_c)$ is negative for small ions means that the effect of these ions in solution is to reduce the diamagnetic susceptibility of the water.

Values of C as given by Bernal and Fowler(17) and values of $(\chi_s'-\chi_c)/C$ are given in the last two columns of table 3. It should be noted that the values given for C represent the maximum number of water molecules which will form a quasi-stable system round a dissolved ion. From an examination of the strengths of solutions used in measuring the susceptibilities of dissolved salts it is found that in all cases the ratio of the number of water molecules to the number of dissolved ions is sufficiently large for each ion to be surrounded by a fully coordinated group of water molecules.

If the values of $(\chi_s'-\chi_c)/C$ can be taken as approximating to $\Delta\chi_w$, then the figures in the final column of table 3 are to be compared with the susceptibility 12·96 of pure water. The maximum negative value of $\Delta\chi_w$ is of the order of 0·8 to 0·9 (the slightly larger value 1·2 for Zn^{+2} is not very reliable) which indicates a change of about 6 or 7 per cent in the susceptibility of the water in contact with the dissolved ions.

The effect of the neglected term $(\Delta\chi_0^c-\Delta\chi_0^s)$, which may be important for large and singly charged ions, can now be considered. From the discussion in previous papers 16) it appears that the susceptibility of an ion decreases numerically with an increase in the co-ordination number. For large univalent ions the co-ordination number in solution, according to Bernal and Fowler(17), is 4, and in crystals of the rocksalt type is 6. We therefore expect $\Delta\chi_0^c$ to be numerically greater than $\Delta\chi_0^s$ and the term $(\Delta\chi_0^c-\Delta\chi_0^s)$ to be positive. Writing out the full expression for $\Delta\chi_w$, we have

$$\Delta\chi_w=(\chi_s'-\chi_c)/C-(\Delta\chi_0^c-\Delta\chi_0^s)/C \qquad \text{......(7)}.$$

Reference to table 3 shows that for large univalent ions the term $(\chi_s'-\chi_c)/C$ is positive. Hence for these ions $\Delta\chi_w$ will be negative only if the second term in equation (7) is numerically greater than the first, i.e. only if

$$(\Delta\chi_0^c-\Delta\chi_0^s)>(\chi_s'-\chi_c).$$

This cannot be tested very exactly, but there are sufficient data to enable an estimate of the magnitude of $(\Delta\chi_0^c-\Delta\chi_0^s)$ to be made for the ions Cl^-, Br^- and I^-. From a study of these ions in the crystalline state we have obtained* their susceptibilities in crystals where the coordination numbers are 6 and 8; the values are as follows, where in each case the larger of the two values corresponds to a co-ordination number 6: Cl^-, 24·2 and 22·9; Br^-, 34·5 and 33·4; I^-, 50·6 and 48·8. If the change in susceptibility in going from coordination number 6 to coordination number 4, i.e. in solution, is assumed to be comparable with the change in going from coordination number 8 to coordination number 6, then we see that $(\Delta\chi_0^c-\Delta\chi_0^s)$ will be of the order of 1·3 for Cl^-, 1·1 for Br^- and 1·8 for I^-. The corresponding values of $(\chi_s'-\chi_c)$ from table 3 are 0·9 for Cl^-, 1·9 for Br^- and 3·6 for I^-. Hence, in all three cases, $(\Delta\chi_0^c-\Delta\chi_0^s)$ is comparable with $(\chi_s'-\chi_c)$, but only in the case of Cl^- is $(\Delta\chi_0^c-\Delta\chi_0^s)$ greater than $(\chi_s'-\chi_c)$. Too much reliance cannot be placed on these differences of susceptibilities, however, which are only small percentages of the actual susceptibilities. The evidence is sufficient to show that, for large univalent ions, $(\Delta\chi_0^c-\Delta\chi_0^s)$ is comparable with $(\chi_s'-\chi_c)$ and hence that $\Delta\chi_w$ is small for these ions. Alternately we may say that the positive values of $(\chi_s' - \chi_c)$ given in table 3 for the large univalent ions arise more from the change in coordination of the ions when they are dissolved than from the effect which these ions have on the water molecules.

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* See reference (16*c*), table IX on p. 405.

The magnitude of the effect of the ions on the water molecules will depend on the field produced by the ions. Since diamagnetic susceptibilities depend largely on the electron-distribution at large values of the radius, it is of interest to consider $\Delta\chi_w$ in relation to the field at the boundary of the ions. If R is the packing radius of an ion as obtained from crystal-structure data, and n the charge in electron units, the field at the boundary will be given approximately by n/R^2. In table 3 the ions are arranged in order of the quantity n/R^2; the values of R are mainly those of Zachariasen. On comparison of the values of n/R^2 and $(\chi_s' - \chi_c)/C$ it will be seen that for the most part there is a progressive change of the latter quantity with n/R^2. This is in accordance with the view that the smaller and more highly charged the ions the greater is their effect on the surrounding water molecules. The only two ions which do not fit into this scheme satisfactorily are Be^{+2} and Li^+. The paucity of experimental data for beryllium salts renders the results in table 3 for Be^{+2} uncertain; this however cannot be the explanation in the case of Li^+.

A few results are included in table 3 for polyatomic ions. These are all approximate, and in the case of the solution values χ_s' there is an additional element of uncertainty arising from the possibility that the salts containing these ions may not be completely dissociated in the solutions used for the susceptibility measurements. For all these ions, however, $(\chi_s' - \chi_c)$ is positive, a fact which is consistent with the positive values obtained for the large monatomic ions. Unfortunately the uncertainty in the values renders any further discussion of little use.

§ 4. THE SUSCEPTIBILITIES OF HYDRATED SALTS

The practice of estimating the susceptibilities of anhydrous salts from the values for hydrated salts has little real justification. In recent years the crystal structures of a number of hydrated salts have been determined in detail, and the results indicate in all the cases yet examined that the water molecules are grouped round the positive ions in a more or less regular manner,* in agreement with the views of Bernal and Fowler. In crystals in which the number of water molecules is sufficient to build up a complete group of coordinated water molecules round the positive ions, the hydrated state resembles a solution more closely than the anhydrous state in so far as the immediate surroundings of each ion are concerned. When the number of water molecules is insufficient to form a complete group, the positive ions in the crystal are only partially separated from the negative ions by intervening water molecules.

In view of these results, it is to be expected that the diamagnetic susceptibilities of hydrated crystals will approximate more closely to the values obtained for solutions than to those for anhydrous crystals. In order to test this expectation a careful search was made through the literature for substances whose susceptibilities have been measured in the three states, anhydrous, hydrated, and dissolved. It is only for relatively few substances that such measurements have been made, but the results available tend to support the above view. New determinations were made for the substances listed in table 4 by the method previously described(16a).

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* The following are typical examples: Hexahydrates of $MgCl_2$, $MgBr_2$, $CrCl_3$, $AlCl_3$, and of the halides of Ca, Sr and Ba; the alums; $CuCl_2 . 5H_2O$; $NiSO_4 . 6H_2O$; $NiSO_4 . 7H_2O$; $H_3PW_{12}O_{40} . 29H_2O$; $3CdSO_4 . 8H_2O$.

Table 4

Salt	Susceptibility of hydrated salt	Calculated susceptibility of anhydrous salt assuming that $\chi_w = 12{\cdot}96$
$MgCl_2.6H_2O$	128·1	50·3
$CaCl_2.6H_2O$	132·1	54·3
$BaCl_2.2H_2O$	98·5	72·6
$SrBr_2.6H_2O$	160·4	82·6
$BaBr_2.2H_2O$	119·3	93·4

In table 5 are compared the susceptibilities of various salts as obtained by the three different methods, i.e. directly from measurements on anhydrous salts, from measurements on hydrated salts assuming the susceptibility of water to be 12·96 per gram-molecule, and from measurements on solutions again assuming the susceptibility of water to be 12·96. The values obtained from hydrated salts in this table without a reference number are from table 4; values obtained from salts in solution are taken from table 1, while the results for anhydrous salts are those we have recently obtained(16c).

Table 5. Comparison of susceptibilities

Salt	Susceptibility			
	Anhydrous	Hydrated	Degree of hydration	Dissolved
$MgCl_2$	49·2	50·3	6	49·7
$CaCl_2$	54·7	54·3	6	56·0
$SrBr_2$	78·9	82·6	6	87·7
$BaCl_2$	72·3	72·6	2	76·4
$BaBr_2$	88·6	93·4	2	100·7
BaI_2	124·4	137·1(19)	2	137·8
$CdCl_2$	68·7(18)	73·1(18)	1	72·3(20)
$CdBr_2$	87·2(18, 8)	93·0(4)	4	92·1(8)
$Cd(NO_3)_2$	55·1(18)	62·7(18)	4	62·3(4)
$CdSO_4$	59·2(18)	61·4(18)	8/3	—
		64·3(18)	1	—
$Cd(CH_3COO)_2$	83·7(18)	84·3(4)	3	—

For the six halides of Mg, Ca, Sr, and Ba the experimental results for the anhydrous and hydrated salts have been obtained mainly with the same apparatus used under standard conditions, and the results for the dissolved salts are averages of the results obtained by several investigators. As a whole these results are probably more certain than those given in the second part of the table.

A comparison of the values in the different columns of table 5 confirms the anticipated result that hydrated salts give for the susceptibility of the salt itself values approximating more closely to the values for the dissolved salts than to those for the true anhydrous salts. In some cases, such as that of $CdCl_2$, in which the number of water molecules is small, the close agreement between the results for the hydrated and dissolved salts is probably to some extent fortuitous. In every case except that of $CaCl_2$ the value is higher for the hydrated salt than for the anhydrous form; no significance can be attached to exceptional character of $CaCl_2$ because in this case there is little difference between the anhydrous and solution values. On the whole the conclusion may be drawn that susceptibilities estimated from results for hydrated salts fall between the values for dissolved and anhydrous salts, but probably nearer the values for dissolved salts.

§ 5. GENERAL CONCLUSIONS

The analysis of the data given in the foregoing sections leads to the following conclusions:

(i) Diamagnetic susceptibilities of salts in solution are additive within the limits of experimental error.

(ii) The values of the susceptibilities as calculated from measurements upon solutions, assuming the solvent susceptibility to remain unchanged, are different from the values obtained for the same substance in the crystalline form.

(iii) There is a definite effect of the ions upon the susceptibility of the surrounding water molecules. There is a correlation between the magnitude of this effect and the field at the boundary of the ion.

(iv) From the limited data available it appears that susceptibility-values obtained from measurements on hydrated salts are different from the values obtained for anhydrous salts, approximating more closely to the values found from measurements upon solutions.

§ 6. ACKNOWLEDGMENTS

Our thanks are due to Prof. F. H. Newman and Dr E. C. Stoner for their continued interest in this work.

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REVIEWS OF BOOKS

The Newer Alchemy, by Lord RUTHERFORD. Pp. viii + 67. (Cambridge: University Press, 1937.) 3*s*. 6*d*.

This is an account (expanded from the Henry Sidgwick Memorial Lecture delivered at Newnham College in November, 1936) of natural and induced radioactive transformations, with a summary of the more important experimental methods used in their investigation. There are also descriptions of some of the high-voltage devices used for obtaining swift charged particles for disintegrating atomic nuclei.

As would be expected, the treatment is lucid and the tone inspiring. The book is meant for the general reader, but the student beginning radioactivity would do well to read it, as a pleasant means of acquiring the necessary background. There are thirteen fine plates, mainly reproductions of Wilson cloud tracks.

Molecular Beams, by R. G. J. FRASER. Pp. ix + 70. (London: Methuen and Co.) (Methuen's Monographs.) 2*s*. 6*d*.

This is a short, readable and up-to-date account by an author who has had the advantage of working in Stern's laboratory, and who is already known as the author of a larger work (*Molecular Rays*) on the same subject, to which he has been an active contributor. There are four chapters, on molecular beams, gas kinetics, magnetic moments and electric moments respectively. The treatment, from the experimental viewpoint, is as full as can be expected within the obvious limitations of space, and the little book should be very useful to students of physics and physical chemistry. H. R. R.

1. *Kernphysik*, by P. AUGER, G. BERNARDINI, W. BOTHE, J. CLAY, J. D. COCKCROFT, J. R. DUNNING, R. FLEISCHMANN, S. FRANCHETTI, H. GEIGER, H. von HALBAN, Jr., L. MEITNER, M. L. E. OLIPHANT, P. PREISWERK and E. J. WILLIAMS; edited by E. BRETSCHER. Pp. iv + 141. (Berlin: Springer, 1936.) RM. 12.
2. *Die Atomkerne*, by C. F. von WEIZSÄCKER. Pp. viii + 214. (Leipzig: Akad. Verlagsgesellschaft m.b.H., 1937.) M. 14.40.

These are two important additions to the literature of nuclear physics. The first is a collection of papers read at the summer meeting of 1936 in the Physical Institute of the Technische Hochschule, Zürich, by a number of specialists. Each paper gives a summary of recent work in a moderately restricted field, and the editor, Dr Bretscher, has added an introductory chapter designed to link these summaries together as closely as is practicable, and to make the book more acceptable to non-specialists. The summaries and the accompanying bibliographies are excellent, and the book can be warmly recommended to students. The contributions of the British and American specialists are in English, Auger's in French, and the remainder in German.

Von Weizsäcker's book is of an entirely different type. It gives a short, but clear and systematic, treatment of the whole range of nuclear physics, with special insistence on the theoretical aspects of the subject. It is a valuable contribution to a theory which is now at a particularly interesting stage of development, and it may be very profitably read by a student who has already some familiarity with, for instance, the books of Feather and Rasetti and the sections on atomic physics in the Physical Society's *Progress Reports*.

There may be sweeping changes in the next edition of von Weizsäcker's book, but as it stands the volume gives an excellent picture of the present state of nuclear physics, and it is far more than a mere compilation. H. R. R.

Hand- und Jahrbuch der chemischen Physik, Band 9. Abschnit v, *Kernspektren*, by K. Philipp. Pp. ii + 105. (Leipzig: Akademische Verlagsgesellschaft m.b.H., 1936.) M. 11.20.

This monograph is a recent addition to a series that is now well-known to English physicists and chemists. It forms, in fact, a further section of the volume, *Die Spectren*, which includes the two monographs previously reviewed in the present volume of these *Proceedings* (p. 79), namely *Anregung der Spektren* by Hanle and *Molekülspektren von Lösungen und Flüssigkeiten* by Scheibe and Frömel. The numeration of its pages (185–283 and 17–22) is in continuation of that of the monographs named. Its five chapters deal with the theoretical and experimental investigations of α, β and γ radiations, and nuclear spectra, structures and transformation processes. In the text are thirty-three tables of numerical data, forty-two figures and numerous references to original papers. W. J.

Hand- und Jahrbuch der chemischen Physik, Band 8, Abschnitt II, *Lichtzerstreuung*, by H. A. Stuart and H. G. Trieschmann. Pp. ix + 191 + 20. (Leipzig: Akademische Verlagsgesellschaft m.b.H., 1936.) M. 24.

This section of the volume *Licht und Materie* in the same series consists of two monographs of nearly equal lengths. In the first, entitled *Lichtzerstreuung im Gebiete des sichtbaren Spektrums,* Stuart deals with the theories and measurements of light scattering by non-absorbing and absorbing particles, Rayleigh and Raman scatterings by molecules, scattering as a vibration phenomenon in pure liquids and in mixtures, critical opalescence, optical anisotropy, etc. The second monograph, entitled *Kohärente Streuung von Röntgenstrahlen an Atomen und Molekülen*, is by Trieschmann. He first discusses X-ray scattering by a free electron, a single atom, gases (both atomic and molecular), liquids and solids; and then describes the experimental methods and results of investigations of charge distribution in atoms, and of investigations of molecular structure. Appended to this monograph are three tables of (i) internuclear distances of atoms in molecules, (ii) atom factors by James and Brindley and (iii) four-figure values of sin x/x by Sherman. Both monographs contain figures, tables of numerical data and numerous references to original investigations, and are adequately indexed. W. J.

Collisions of the Second Kind, their Rôle in Physics and Chemistry, by E. J. B. Willey. Pp. viii + 150. (London: Edward Arnold and Co., 1937.) 10*s*. 6*d*. net.

In this monograph the author describes how Franck's general theory of collisions of the second kind has been invoked in the last ten or twelve years to explain many phenomena the origin of which would otherwise have remained obscure. Following an introductory chapter there are five chapters dealing with excitation of spectra, ionization by electron transfer, collisions of the second kind at gas-solid interfaces, the quenching of resonance radiation, and chemical reactions involving collisions of the second kind. In view of the wide range of topics discussed, from spectroscopy to chain reactions with sections touching on thermionics and biology, the author has adopted a descriptive rather than a critical style, leaving the reader, with the aid of an extensive bibliography, to form his own conclusions where differences of opinion exist. It is regrettable, however, that he has kept so closely to this style, as to leave the reader to transcribe the spectroscopic terminology used in many of the original papers cited into that more recently and widely adopted. This matter, as well as the correction of several misprints, should receive careful attention in a future edition.

W. J.

Anleitungen zum Arbeiten im Röhrenlaboratorium, by M. KNOLL. Pp. ii + 67. (Berlin: Springer, 1937.) RM. 3.

This—the third part of a manual of experimental electrotechnics begun some years ago by the late Dr E. Orlich—deals with thermionic tube (including vacuum) technique. The contents are arranged as a set of fourteen laboratory exercises, each of which is intended to keep the student occupied during a 4-hour period. The exercises range from the calibration of vacuum gauges to work with an electron microscope.

The course was developed in the Technische Hochschule, Berlin. In all probability, few English readers will follow out the complete course in this form, but many will find in this little book a very useful collection of practical hints. H. R. R.

Electrical Measurements, by H. L. CURTIS. Pp. xiv + 302. (London: McGraw-Hill Publishing Company, 1937.) £1. 4*s*.

This is not a laboratory manual of the usual type; its aim is sufficiently well indicated by the sub-title "Precise Comparisons of Standards and Absolute Determinations of the Units", and by this significant sentence in the preface: "The discussion of the methods is based on the assumption that an accuracy of one part in a million is desirable in every type of measurement."

Thus warned, the reader will not look for information on "Resistance of a cell; Lodge's modification of Mance's method"—he will not even find the Carey-Foster bridge, though he will find the Kelvin double bridge. What he will find—and what will be of the greatest use to the majority of readers—is an admirable critical, and in part historical, account of methods which have been used, or may be used, to establish the electrical units with the highest attainable precision. Some knowledge of these methods is required by every serious student of physics, even though he himself may never be called upon to measure any electrical quantity with an accuracy better than one part in ten thousand.

In addition to experimental details concerning the realization of the units and the comparison of standards, there are valuable sections on the computations of fields and inductances. As Principal Physicist at the Bureau of Standards, and a former collaborator with the late Dr E. B. Rosa, Dr Curtis is obviously able to write with authority on these topics, and he is to be warmly congratulated on the production of this book, which is a notable addition to that notable Series—The International Series in Physics. H. R. R.

Alternating Current Measurements, by D. OWEN. Pp. vi + 120. (London: Methuen and Co.) 3*s*. 6*d*. net.

This, one of Methuen's Monographs on Physical Subjects, shows a rather more practical bias than some of the recent items which have appeared. It falls roughly into three sections, of which the first deals with bridge methods for the measurement of inductance and capacitance. The various bridges are dealt with, using a consistent method of expressing the theory, and thus making the book easier to study, and rendering comparisons between the different bridges easier to make. An extremely valuable addition to this section forms the fifth chapter, and deals with the conditions of accuracy in bridge measurements. The numerical effects of the residual components in the impedance of a quantity which is intended to function either as a pure resistance, pure inductance or pure capacitance are considered, and the Wagner earthing device is both described and explained.

The second section is devoted mainly to short but satisfactory explanations of both the polar and rectangular co-ordinate types of a.-c. potentiometer, and includes also Robinson's method of measuring frequencies by means of a modification of Wien's bridge.

In the final section, attention is directed chiefly to resonance methods of measuring inductance, capacitance, resistance and frequency at radio-frequencies. A useful and well worded reminder is given that the first three of these quantities are themselves functions of frequency, and must therefore be measured under operating conditions. Moreover, for an impedance which is not purely one of the three, its effective value is what is measured—and may sometimes, though not always, be the quantity required.

Although it is easy to outline the contents of the book (and indeed easy to read it), it can have been no easy task to write it. The difficulty of lucid expression increases within limits with the compression imposed, but in this case, any difficulties which may have been encountered, have been overcome so skilfully that the reader fails to notice where they may have been. J. H. A.

Über einige neuere Fortschritte der Additiven Zahlentheorie, by E. LANDAU. (Cambridge Tracts in Mathematics and Mathematical Physics, No. 35.) Pp. ii+94. (Cambridge: University Press.) 6*s*. net.

Natürlich kann dieses Buch die ganze Primzahlentheorie nicht enthalten, sondern es ist auf einige der neuesten Entdeckungen beschränkt. Es entsteht aus einer Reihe von vier Vorträgen, die der Schriftsteller in Cambridge gehalten hat, und es besteht folglich aus vier Kapiteln, die die Sätze von Winogradoff, Schnirelmann, Erdös und Romanoff, und Khintschine, Besicovitch und Tchowla behandeln, nebst einem Anhang, welcher einen Satz von Siegel enthält. Am Anfang findet man eine kurze Übersicht, die den Inhalt jedes Kapitels erklärt.

Die Theorie ist ziemlich schwierig, aber der Leser der sich nicht erschrecken lässt, wird sie für höchst interessant halten. Er wird auch einige Probleme zur Forschung entdecken.

Wie die andere "Cambridge Tracts" ist das Buch ausserordentlich gut gedruckt. Es kostet mehr als Nummer 34, aber mit Rücksicht auf der Schwierigkeiten, mathematische Formeln zu drucken, ist es gar nicht teuer. J. H. A.

The Elements of Mathematical Analysis, by J. N. MICHELL and M. H. BELZ. Pp. xxiii+516 (vol. 1) and xii+570 (vol. 2). (London: Macmillan and Co.) 42*s*. net each volume.

This is a most interesting essay in a systematic unfolding of the fundamentals of analysis according to modern principles. It could be attacked by a student who has a moderate knowledge of algebra and (geometrical) trigonometry, and would leave him with nothing to unlearn when he came to modern advanced treatises. Volume 1 is devoted to the differential calculus, which is treated, as far as subjects and applications are concerned, in a manner reminiscent of the Williamson of last generation, although the similarity only emphasizes the difference in underlying treatment. The method of sections and the use of nests of intervals to define a number, are not only explained, but actually used. In general, in fact, the volume is a text on the properties of sequences—as it ought to be—and there is only a passing reference to the properties of series and their convergence. The subject of the complex variable is not taken up.

There is a claim that the book is adapted to the particular needs of students of science and engineering, and it is impossible to disprove such a claim until the book has been tried with classes, but one feels that in general the needs of the student of applied science are somewhat different from those catered for here. Thus, the practical man is usually satisfied with the degree of rigour that can be attained by assuming the intuitive properties of curves: if he uses numerical methods to solve equations he would often prefer iterative methods (which are quite ignored), to Newton's method of applying a correction. These methods are useful in practice, and would illustrate well the subject in hand, since the theory is that of the convergent sequence; moreover, unlike Newton's method, the margin of error can be assessed without heavy arithmetic.

The second volume, dealing with integral calculus, has the same general features as the first as regards rigour. The treatment of lengths and areas, particularly the areas of the surfaces of solids, is thus rather more difficult than is usual in books of this standard, though the examples chosen for treatment are of quite normal type. This volume contains an excellent chapter on numerical integration, which might have been even more valuable if it had pointed out that expansion in series is often the best method of all. It is true that such expansions have been dealt with earlier, but the student could hardly be expected to remember them in this connexion, unless his attention is specially directed to the point.

A distinct innovation is a chapter on the methods of moments and of least squares in curve-fitting, but this again (perhaps justifiably) dismisses very briefly the problem where the given function is represented by a table and not by a formula. The opportunity is taken to introduce zonal harmonics in a rather novel way in this chapter. The book concludes with a short course on ordinary differential equations treated in a conventional manner.

The departures from standard nomenclature are rather numerous, and many of them are probably improvements. Among them we may note "barrier" for "bound", "arsin" for "arcsin", "$ex \sin c\,(kx, \alpha)$" for "$e^{kx\cos c} \sin(kx \sin c+\alpha)$" and the introduction of a name and symbol for the function which equals $\cosh\sqrt{h}$ when $h>0$ and $\cos(x\sqrt{-h})$ when $h<0$, and for the function equal to $(x\sqrt{h})^{-1}\sinh(x\sqrt{h})$ or to $(x\sqrt{-h})^{-1}\sin(x\sqrt{-h})$, according as h is greater or less than zero.

The book is well printed and bound, and is provided with an excellent index. Even so, four guineas seems rather a high price, and one that will make many a student hope that it will not be selected for his course of lectures. J. H. A.

Elementare Physik, by ARTHUR HAAS. Pp. x+204, with 85 figures in text. (Vienna: Julius Springer, 1937.) RM. 4.80.

This little book makes no claim to be regarded as a textbook, but is intended to supply a concise survey of the most important problems and results in experimental physics for those who have already done an elementary course and wish to continue their reading. This purpose it should serve admirably. It is divided into four parts dealing, respectively, with mechanics and acoustics (49 pages), heat (23 pages), optics (46 pages) and electricity (72 pages). The variety of the topics included in each part is far too wide for description in this short notice; the treatment of most of them is necessarily very brief, and no higher mathematics is invoked. Two errors have been noticed which the brevity and elementary nature of the treatment in no way explain or excuse: in figure 48 (b and b'), illustrating long sight and its correction, the incident rays of light are indicated as coming from a far distant, instead of a near, object; and on p. 138 the kilowatt-hour is defined as the work done by a current of 1 watt in 1000 hours, although the watt is correctly defined a few lines before. W. J.

Contributions from the Physical Laboratories of Harvard University for the Year 1935. Series II; Vol. II. (Cambridge, Mass., and London (Humphrey Milford), 1937.) 10*s*. 6*d*.

This handsome volume, containing 57 papers, arranged alphabetically under authors and beginning with five (aggregating 84 pages) by Bridgman, forms a most impressive record of a year's output from the Harvard Physical Laboratories. The range of topics is very wide, and in this age of specialization it must be of immense cultural value to the young physicist at Harvard to see such varied types of research in progress—but again, in this age of specialization, there must be very few readers who are equally interested in (for instance) the high-pressure work of Bridgman and the magnetic work of Van Vleck, important though these both are. Furthermore, with the exception of a short paper by Chaffee from the *New England Journal of Medicine*, all the papers are readily accessible to English readers—nearly half are from the *Physical Review*. There seems therefore to be no particular reason, apart from a special interest in Harvard, why many readers should wish to possess the complete collection in this form. H. R. R.

Zero to Eighty. by AKKAD PSEUDOMAN (E. F. NORTHRUP). Pp. viii + 284. (New York: The Scientific Publishing Co.) $3.50.

Dr Northrup has been experimenting with "electric guns" which are essentially solenoids placed end to end and operated by polyphase a.c. in such a way that a magnetic field travels continuously along the axis at high velocity, and pulls a metal object along, so that it leaves the tube at enormous speed. He believes that with a gun of this nature it would be quite feasible to project a vessel in which men might travel around the moon, and return to earth. In order to convince the world of this, he has chosen to present his case in the form of an autobiography written in the year 2000 A.D. by Akkad Pseudoman, an individual who was born in 1920, and made the flight in middle age. The arguments are plausible, perhaps convincing, even though we may doubt the validity of the method which he outlines for steering. After all, there are others available, of which the simplest is a system of rockets directed outwards along the principal axes of the momental ellipsoid of the vessel.

A book written in this way naturally invites—or demands—comparison with its numerous predecessors in the field of scientific romance, and it emerges pretty well from the ordeal. The characterizations may be weak—Pseudoman's wife, who was such an inspiration and a help to him, is the central figure in one chapter, and yet is a shadowy, unreal figure even to the end of the book. Still, the same fault is shared by better-known writers; Mr Britling and Mr Lewisham are more real persons than he who ate the Food of the Gods or than that other who travelled with the Time Machine: Micah Clarke and Dr Watson have more humanity than the professor who found the Lost World.

On the other hand, the professional writers who have peeped into the future, have usually succeeded in mentioning some changes—in roads, clothes, food, reproduction or what-not—which strike the reader with surprise, because he had not thought of it himself. Admittedly, this book only extends 63 years from to-day, but one might have hoped for more changes. True, the aeroplane is the common mode of travel, with stratospheric flight for inter-continental voyages, and a televisor is attached to the telephone. But the economic system is apparently unaltered, gold has its outstanding place among commodities, gangsters can still be found in the U.S.A., the American language has stood still (save that the irritating growth which occurred in the late 30's, typified by the statement "we have thus proved *rather definitely* that the theory is correct", has disappeared), Russia is still the most progressive nation, and American students still "elect" subjects and collect "credits". (Young Pseudoman's decisions as to his course of study remind the English reader irresistibly of Stephen Leacock's student who, because the time of day suited him, elected Music, Religion, and Turkish, to the bewilderment of one of his acquaintances, who assumed that he must be preparing for a life as organist in a mosque).

The lay reader will presumably judge the book from this aspect of entertainment value, and will find that, though not in the front rank, it is a sound piece of workmanship, better conceived than at least half the detective novels and written in better English. The price, which is probably raised considerably by the many plates, will put it out of reach of many on this side of the Atlantic. J. H. A.